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Electrochemical Reduction of 2-Methylcyclohexane-1, 3-Dione at Stainless Steel (Ss-316) Electrode in Basic Media

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ABSTRACT: Cyclic voltammograms of 2-Methylcyclohexane-1, 3-dione were recorded at different pH (4.0, 7.0, & 9.0) to establish the optimum conditions its the reduction. The Galvanostatic reduction of 2-methylcyclohexane-1, 3-dione was thereafter carried out galvanostatically at pH = 9.0 using Stainless Steel (SS-316) as a working electrode. The good yield (88.8%), of 3-hydroxy-2-methyl cyclohexanone was obtained, which was isolated and purified by chromatographic techniques and characterized on the basis of spectral analysis.

KEYWORDS: 2-Methylcyclohexane-1, 3-dione, Galvanostatic reduction, Stainless Steel (SS-316) Electrode, Cyclic Voltammetry,

I. INTRODUCTION

There are several characteristic features of electro synthesis which are cited quite often. Firstly, electron flowing as current may be regarded as one of the reagents. Secondly, in electro-organic synthesis these reactions may take place in a low temperature, which reduces the local consumption of energy and also the risk of corrosion, material failure and accidents. These reactions can also be carried out in low-volatility or no- volatility reaction media. In these cases, the electrodes may be regarded as heterogeneous catalysts that are easily separated from the products and finally the overall reaction conditions are ecofriendly [1].

Aldehydes and ketones have been found to undergo electrochemical reduction easily [2-3] to the corresponding alcohols [4]. The course of reduction of aldehydes and ketones is strongly dependent upon the pH of the medium. The electrochemical reduction under acidic conditions yields pinacols, while under basic conditions corresponding alcohols are formed. [5].

The present research is aimed to investigate electrochemical reduction of 2-Methylcyclohexane-1, 3-dione in basic medium using SS electrode at constant current so as to develop an effective, ecofriendly, synthetic procedure because its reduction product, 3-hydroxy-2-methyl cyclohexanone, is extremely useful as a building block in terpene synthesis [6].

II . MATERIALS AND METHODS

All chemical used viz. sodium acetate, sodium hydroxide, 2-methyl-1, 3-cyclohexanedione, etc. were of AR grade. The solutions were prepared in triply distilled water. Cyclic Voltammetric studies were carried out in a three electrode cell assembly using 1mm diameter glassy carbon as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode.

Preparative electro-organic synthesis, utilizing the optimum conditions derived from cyclic voltammetric studies was then carried out at pH = 9.0. The conventional H-type cell with two limbs separated by G-4 disc was used for electrolysis. The supporting electrolyte sodium acetate (250 ml, 1M) was filled equally in both the limbs. 2-methyl-1, 3-cyclohexanedione (5.0466 gm) was dissolved in the alcohol and placed in the cathodic chamber.

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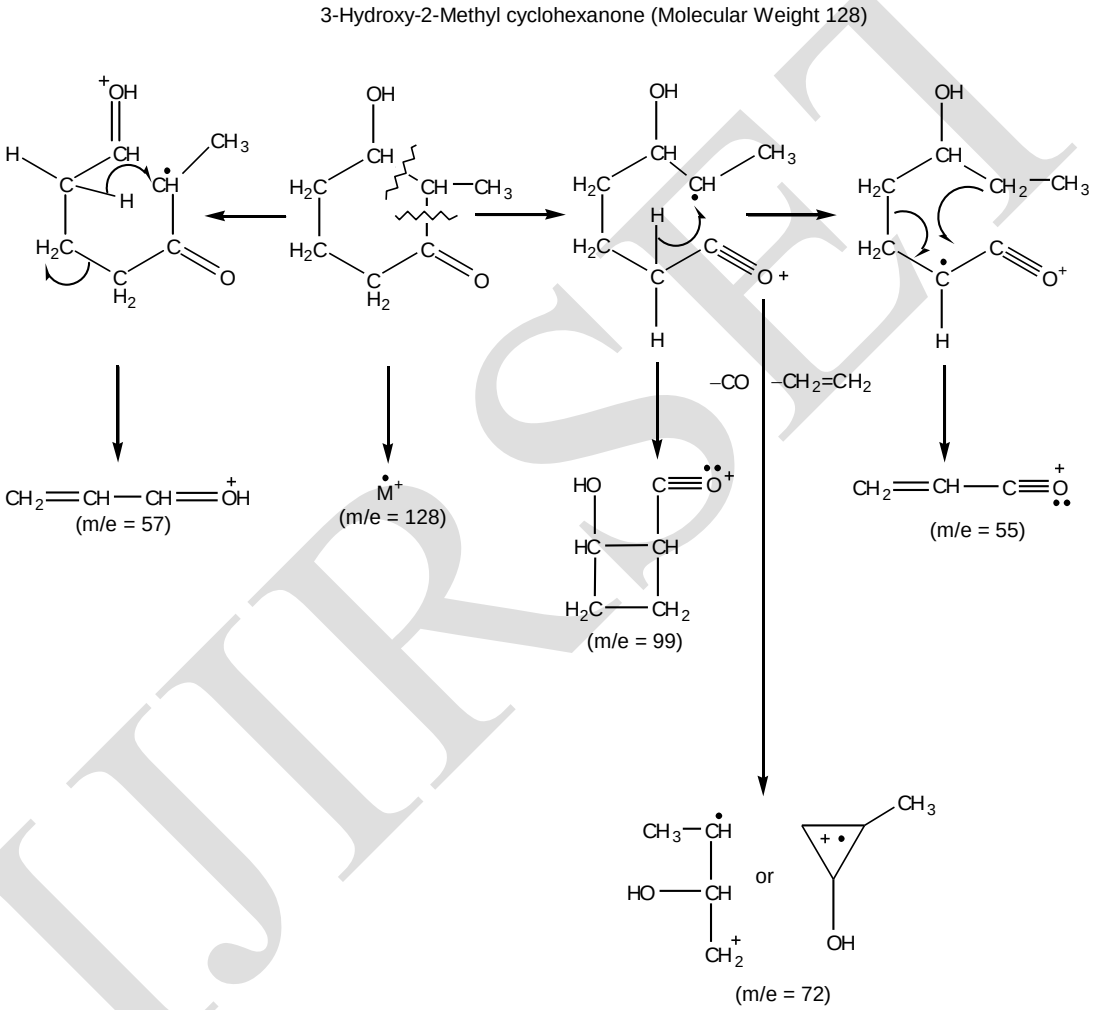
The Stainless Steel (SS 316) electrodes [7-12] having an area 2 x 3 cm^2 were used as cathode as well as anode. The constant current (1 amp.) was passed through the electrotype for 8 hours with the help of Galvanostat (Prepared by Centre for Development of Physics Education (CDPE) University of Rajasthan Jaipur).

After the completion of the reaction the resulting mixture was filtered. The water was removed from the solution by distillation. The residue was then extracted repeatedly with diethyl ether. The ether layer was allowed to evaporate. After evaporation product was isolated, purified and characterized by combined application chromatographic techniques and spectroscopy viz. IR, NMR (^1H, ^{13}C), Mass details given in Table 1 and scheme 1.

Scheme1: Mass spectroscopic analysis



III RESULTS AND DISCUSSION

The voltammographic curves of 2-methyl-1, 3-cyclohexanedione 0.1M in aqueous medium, potassium chloride 1M as supporting electrolyte and BR buffer (pH= 4.0, 7.0 and 9.0) at glassy carbon electrode using Ag/AgCl as reference electrode are recorded.(Figure 1).

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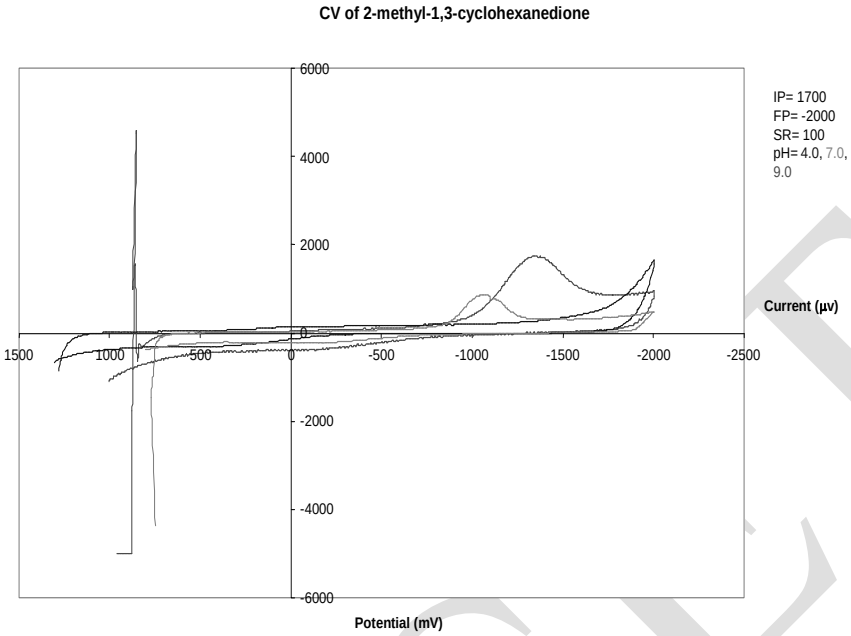

Figure1: Cyclic voltammogram of 2-methyl 1,3-cyclohaxanedione at different pH 4.0,7.0 and 9.0

The cyclic voltammograms were recorded with an initial potential Ei on 1700mv and final (switching) potential Es on –2000mv at different pH and at same scan rate i.e. 100 mV/sec. in aqueous medium.

These studies also lead to the conclusion that reduction can be best carried out in basic media due to these reasons:-

1. In acidic media there is no peak, whereas in neutral media less defined peak but in basic media a prominent peak is appeared.
2. Stainless steel (SS-316) electrode can be easily used as cathode, in basic media due to its corrosive tendency in acidic media.
3. The reduced product 3-hydroxy-2-methyl cyclohexanone (B.P. =163^{o} C reported 161^{o} C) was obtained in reasonably good yield. (Single spot) TLC (Rf =0.5925) was used to check the purity of compound.
4. On the basis of the cost of product and the reactants this electrochemical transformation is economically viable and has potential of scaling up the process for which further studies are in progress.

The identity of 3-hydroxy-2-methyl cyclohexanone was further confirmed by spectroscopic analysis. (Table 1).

Table: 1 Spectroscopic Analysis (IR, ^{1}H, ^{13}C, Mass specta) of the confirmed product

B.P. (^{0}C)	IR Data (cm^{-1})	NMR Data (δ value)	Mass Spectra (m/z)	Compound confirmed	^{13}C NMR (δ value)	Yield (%)
163	3300-3450 2931 1655 1384-1260 1196	1.14 (3H) 1.8 (1H) 2.1 (2H) 2.3 (2H) 2.6 (2H) 3.9 (1H) 2.3 (OH)	55 57 72 99 128	3-hydroxy- 2-Methyl cyclohexanone	210 33.1 69.8 35.5 25.3 41.8 23.7 39.7	88.8

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IV. CONCLUSION

On the basis of the cost of product and the reactants this electrochemical transformation of 2-methylcyclohexane-1, 3-dione at stainless steel (ss-316) electrode in basic media, is economically viable.

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