Electrolytic Reduction of Cyclohexanone to Cyclohexanol at Lead, Amalgamated Lead, Copper and Amalgamated Copper Electrodes

P. L. SHARMA AND J. N. GAUR
Chemical Laboratories, University of Rajasthan, Jaipur - 302 004

THE electrolytic reduction of cyclohexanone at lead and amalgamated lead cathode was studied in aqueous acidic medium. The results under similar conditions were compared with copper and amalgamated copper electrode. The product isolated was identified as cyclohexanol.

THE electrolytic reduction of ketones has been studied extensively by polarographic methods[1-7]. It has been shown that there are two possible reduction mechanisms, depending upon pH. At sufficiently low pH (pH < 6), the reduction product is the alcohol, while at sufficiently high pH (pH > 8), formation of free redicals and dimerization of the same takes place[8-10]. Allen and Corwin[11], Pasternak[9] have proposed similar theory for the reduction of ketones. Emphasis was given to experimental condition chosen. Ordinary temperature, suitable current densities facilitate the reduction of ketone to alcohol under galvanostatic conditions.

Anziani and coworkers[1] electroreduced 2-Methyl cyclohexanone to 2-Methyl cyclohexanol at copper and nickel electrodes in acidic medium at room temperature (25-30°C). Similarly Tomilov[12] and Ignateva[13] studied the electrolytic reduction of aliphatic ketones in alkaline medium at Pb, Tl and Zn electrodes, getting both alcohol and pinacol. In the present communication, the reduction of cyclohexanone is studied at lead, amalgamated lead, copper and amalgamated copper cathodes in aqueous acidic medium at room temperature (25-28°C). Attempts were made to obtain cyclohexanol by the proper control of current density, temperature and acid strengths.

EXPERIMENTAL

Materials and Apparatus :

Chemicals : Cyclohexanone, sulphuric acid and mercuric sulphate used in the study were all BDH, AR grade chemicals.

Apparatus : The cell assembly employed was a 500 ml beaker. Proper arrangements were made for setting porous pot, stirrer, thermometer, cathode and luggin capillary (agar-agar bridge) to measure the cathode potential via reference electrode (SCE). The desired current for electrolysis was passed from a constant current regulated power supply (0-10A) and (0-50V) and cathodic potential was measured with an electronic voltmeter during electrolysis.

Proceduce : A sample of 5.00 gm (5.3 ml) of cyclohexanone in 250 ml 5% H_2SO_4 solution was used as catholyte. A lead strip ($8 \times 2 = 16$ cm^2) was used as cathode. Anolyte 10% H_2SO_4 with lead electrode was set up in porous pot. The electrolysis was carried out till a total current equivalent of 2F/mole was passed and stirring of the catholyte was maintained by a glass stirrer.

Isolation and Identification : After electrolysis, the catholyte was treated with a saturated solution of sodium bisulphite. The solution was filtered off to recover any unreduced ketone as the addition compound ; filtrate was treated with ether three times. The ether extract was dried over anhydrous sodium sulphate to remove moisture, if any from the end product. The liquid product was identified as cyclohexanol by the following physicochemical tests :

(1) Its boiling point was found in the range of 160-162°C. The b.pt. of cyclohexanol is 161°C.

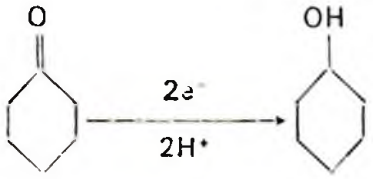
(2) With 2,4-dinitrophenylhydrazine reagent, a negative test indicated the absence of any Ketonic group in the compound.

(3) Final confirmation of the product was drawn by IR spectra in neat form recorded on Perkin-Elmer model 577. The absence of C=O group peaks in the region 1600-1700 cm^{-1}, and appearance

of a broad band due to -OH group between 3450-3250 cm^{-1} and sharp peaks due to $-CH_2$ along with its side band at 2950 cm^{-1} and 2890 cm^{-1}, confirms the compound to be cyclohexanol.

RESULTS AND DISCUSSION

The electrolytic reduction of cyclohexanone to cyclohexanol can be represented as follows :



This reduction was carried out in acidic medium at lead, amalgamated lead, copper and amalgamated copper cathodes to see the effect of change of electrode under identical conditions. Similarly a few experiments were conducted at different acid strengths at both type of electrodes chosen for study. Polarization studies were performed under all conditions,

Fig. (1) is a plot of cathodic potential vs. log c. d. in the absence and presence of depolarizer in 5% H_2SO_4 at 25-28°C at lead and amalgamated lead cathode. From the curves in fig. (1). it is apparent that the reduction of depolarizer starts at more negative potential than without depolarizer, secondly, the reduction of the compound was found effective at low current densities. In the case of lead cathode the depolarization is good upto 0.5 A/dm^2, a suitable range of current density for alcoholic conversion[14]. Above this, a study state is observed upto 2.5-3.0 A/dm^2; in this range no doubt depolarization occurs but with low current efficiency.

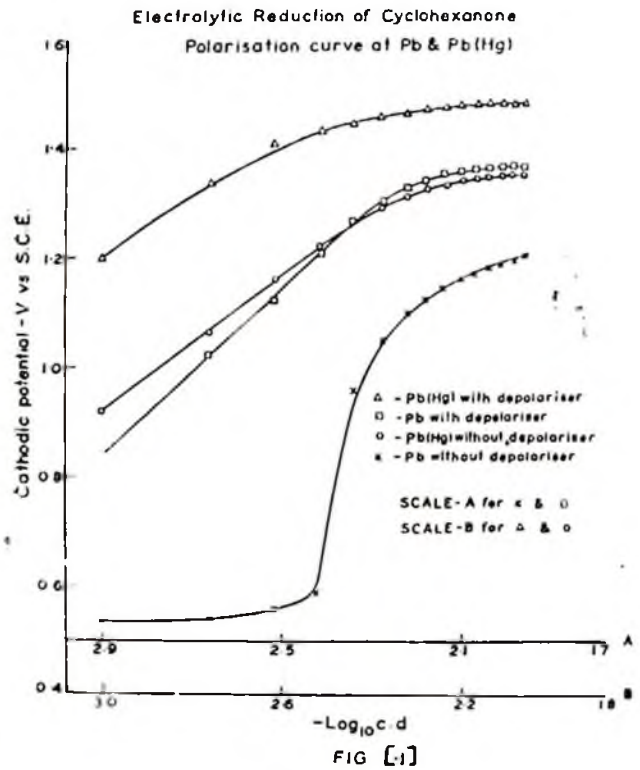


FIG [1]

While the depolarization at amalgamated lead electrode in this range of current density was not found visibly so effective as shown in Fig. (1). In fact, at amalgamated lead cathode. it appears that the process of dissociation of ions from the mercury surface is rather slow enough to take a second proton to give the alcohol in comparison to to the rate of adsorption of ketonic species at mercury surface[15]. Quantitative results obtained at both type of cathodes are presenred in Table 1.

TABLE 1

Cathode : Leadstrip (8x2 = 16 cm^2), amalgamated lead (8x2,5 cm = 20 cm^2), catholyte : 250 ml containing 5% H_2SO_4 and 5.0 gm of cyclohexanol anolyte ; 10% H_2SO_4, anode ; Pb-strip Temperature ; 25-28°C. c.d. = 0.0125 A/cm^2

No. of Expts.	Cathodes	Wt. of cyclo-hexanol obtained	Current Effictency%
1.	Lead	3.48 gm	68.2
2.	Amalgamated lead	2.50 gm	49.0

From the table, it is clear that reduction is quite sensiiive at lead cathode in comparsion to amalgamated lead.

Effect of acid strength : To study the effect of different acid strengths on the electrolytic reduction of cyclohexanone at lead electrode, four sets of acid strength were taken to find most suitable one for highest degree of depolarization. Fig. (2) is a plot of cathodic potential (SCE) vs log of c.d. at 25–28°C in the presence of depolarizer at lead cathode. From the polarization curves as well as from the quantitative results (Table 2), a strength 5% H_2SO_4 was found to most suitable for this reduction under the conditions employed. At higher acid strengths, the current efficiency decreases gradually, probably due to the presence of larger concentration of H^+ ions around the

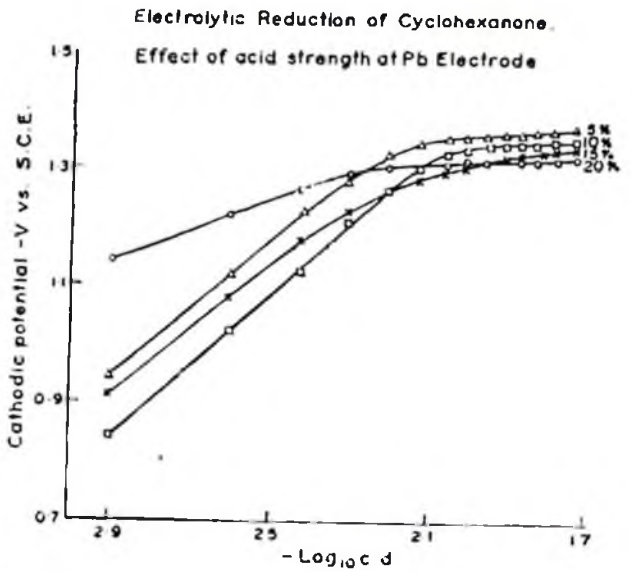


FIG [2]

electrode surface, a major portion of electrical energy supplied is being consumed for their own reduction.

TABLE 2

Cathode : lead sheet (8x2 = 16 cm²), catholyte : 250 ml solution containing 5.0 gm of cyclohexanol + varying% of acid, anolyte : 10% H_2SO_4, anode : Pb-sheet, Temperature : 25-28°C, c.d. = 0.0125 A/cm²

No. of Expts.	Acid strength%	*Wt. of cyclohexanol obtained	Current Efficiency%
1.	5.0	3.48 gm	68.2
2.	10.0	3.20 gm	62.6
3.	15.0	2.72 gm	53.4
4.	20.0	2.35 gm	46.0

*The results are produced in wt. unit rather than volume unit.

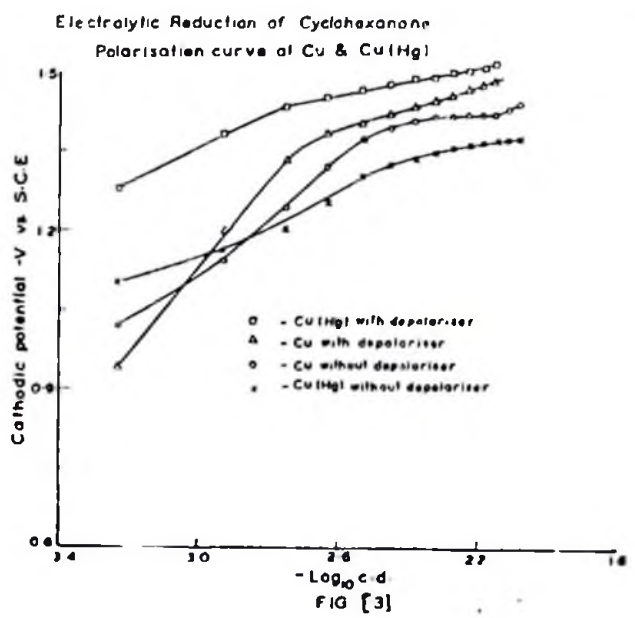


FIG [3]

Effect of change of cathode : To see the effect of change of cathode on this reduction, the investigations were extended at copper electrodes Fig. (3) is a plot for copper and amalgamated copper in 5% H_2SO_4 ; with and without depolarizer From the figure, it is evident that copper is better choice of electrode than Cu(Hg) similar to Pb(Hg). Copper follows the same way as Pb cathode, here at this electrode, the depolarization is good upto 0.3 A dm² (low current density region). However, it also shows a steady state character of depolarization upto 3 A/dm². The quantitative results obtained are presented in Table 3.

TABLE 3

Cathode : solid cylinderical copper rod (h = 8 cm. dia = 1.3 cm = 34 cm²), Catholyte : 250 ml solution containing 5.0 gm cyclohexanol + 5% H_2SO_4, anolyte : 10% H_2SO_4, anode : Pb-strip, Temperature : 25-28 C and c.d. 0.5A/dm²

No. of Expts.	Cathodes	Wt. of cyclohexanol obtained	Current Efficiency %
1.	Copper	3.29 gm	64.5%
2.	Amalgamated Copper	2.35 gm	46.0%

Depolarization curve with time : To understand the course of depolarization with time, the cathodic potential was noted after some interval of time. Fig.(4) is a plot of cathodic potential (SCE)

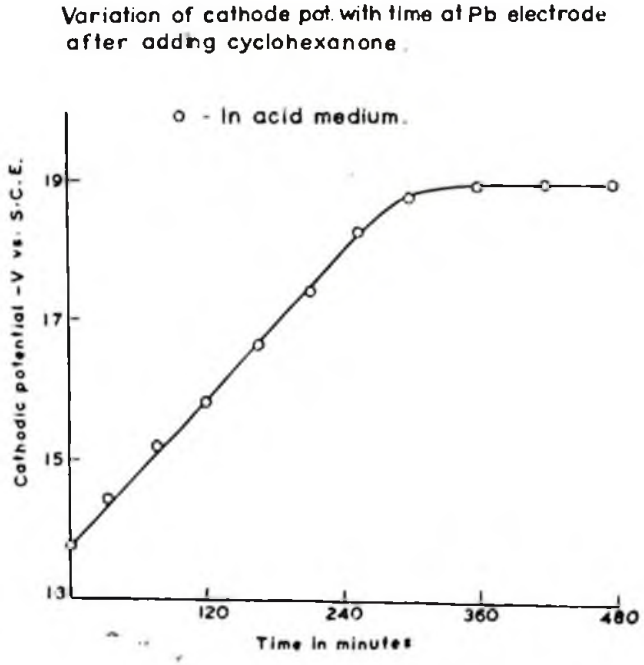


FIG [4]

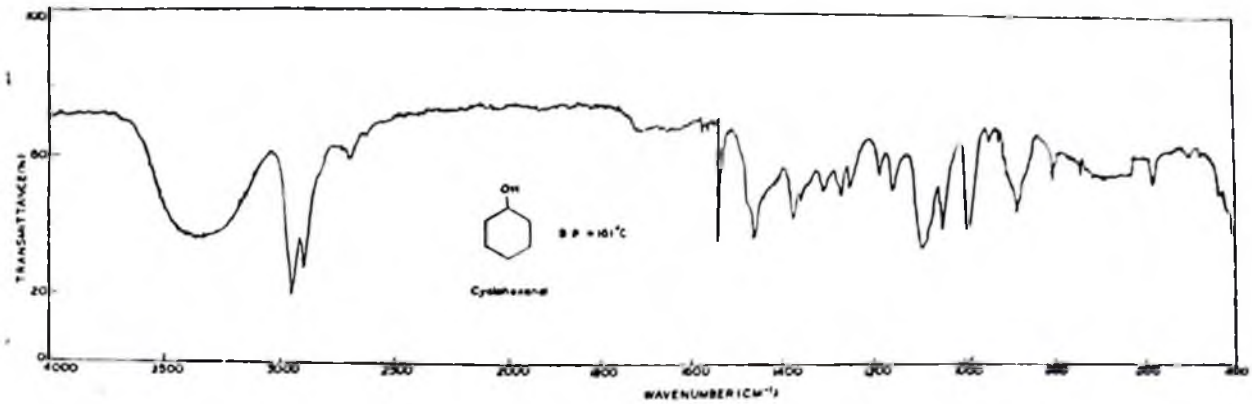


Fig. 5

vs. time in minutes at lead electrode in 5% H_2SO_4 at 25–28°C by taking 3.0 gm of depolarizer at the same current density. The weight of cyclohexanol obtained was 2.068 gm (current efficiency = 67.58%). The reduction was found to follow the theoretical time as required for this transformation, at the end of electrolysis it approaches to limiting value showing the complete conversion into product.

CONCLUSION

From the above mentioned results so obtained under the experimental conditions employed, the results were found better at nonamalgamated electrodes. Lead and copper were found quite sensitive to electrolytic reduction of cyclohexanone in 5% H_2SO_4 medium at low c.d. and room temperature (25–28°C). The reduction was found completed in theoritical time as required.

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