A STUDY OF THE ELECTROCHEMICAL REDUCTION OF CYCLIC KETONES

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The electrochemical reduction of cyclopentanone and cyclohexanone in ethanolic solution (10%) and in the presence of 0.25 N H_2SO_4 has been investigated. The reduction has been carried out at metallurgical copper and electrodeposited cadmium cathodes. The reducibility of the two cyclic ketones was found to be higher in acid medium than that in neutral or alkaline ones. It was noticed that the reducibility of cyclohexanone is higher than that of cyclopentanone under various conditions.

In continuation to our earlier publications [1], here are reported the results of investigation of electrochemical reduction of two cyclic ketones under various experimental conditions.

EXPERIMENTAL

All chemicals used are of AnalaR grade and they are employed without further purification. The electrolytic cell consisted of two compartments separated by a sintered glass.

Copper spiral of 5 cm^2 surface area was etched in acid mixture, cadmium plated [1] and used as cathode. The anode was a platinum sheet. The electrolysis medium was either 0.25 N H_2SO_4 in 10% ethanol(acid) or 0.5 N NaOH or 1.0 N Na_2SO_4 adjusted to pH 7. The temperature was 30 ± 1°C

After electrodeposition process, the cathodes are throughly washed with bidistilled water, then immersed in the electrolytic cell for 15 minutes before switching. The cathodic potentials are measured against a saturated calomel electrode.

RESULTS AND DISCUSSION

It is found that the reduction efficiency of cyclopentanone and cyclohexanone in acid medium varies with the hydrogen overvoltage of the cathode and current density of reduction. The electrolytic cadmium cathode is known to posses the highest hydrogen overvoltage while copper cathode has a considerable low values of hydrogen overvoltage [4]. The efficiency for the reduction of the two ketones at cadmium cathode (performed at 10 mA cm^{-2}) appears to be the highest while at copper cathode, it is the lowest. This is in good accord with the reported behaviour of the different cathodes concerning the reducibility of organic functions [5].

Fig. 1 shows the reduction efficiency over a wide range of current densities. It is seen that the reduction efficiency of cyclohexanone is higher than that of cyclopentanone. In case of cyclohexanone there are six resonating ketoenol structures which are stabilized by hyperconjucation, but in case of cyclopentanone, five resonating structures are available. This could make the reduction of cyclohexanone easier than that of cyclopentanone. Another factor that may be responsible for this behaviour is the polarity of carbonyl group which seem to play a role to some extent. In cyclohexanone the presence of five $-CH_2$ groups may increase the positive charge (δ^+) on carbonyl carbon more than that in cyclopentanone (four $-CH_2$ groups). Consequently, the adsorbability of cyclohexanone may be higher than that of cyclopentanone which is reflected in the ease of reduction. A galvanostatic cathodic polarization curves of the two cycloketones (0.05 M) at copper and electrolytic cadmium cathodes are illustrated in Fig.2. From this figure it is quite clear that the reduction potentials are near the hydrogen evolution potentials on copper cathode while at cadmium cathode the hydrogen evolution process occurs at sufficiently higher cathodic potentials. This explains why the reducibility is low at copper cathode.

The order (n) of the overall electrode process is calculated at different potentials and cited in Table 1 using the power function:

$$i_{(E)} = KC^n$$

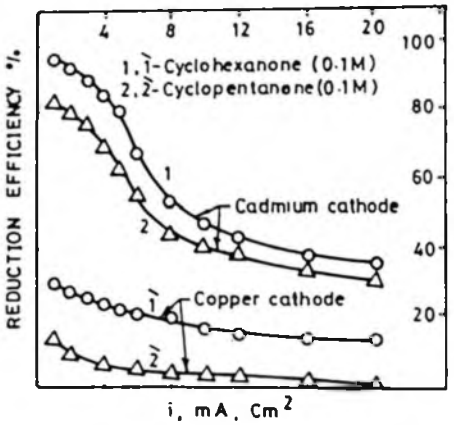


Fig. 1 Reduction efficiency of cyclohexanone and cyclopentanone

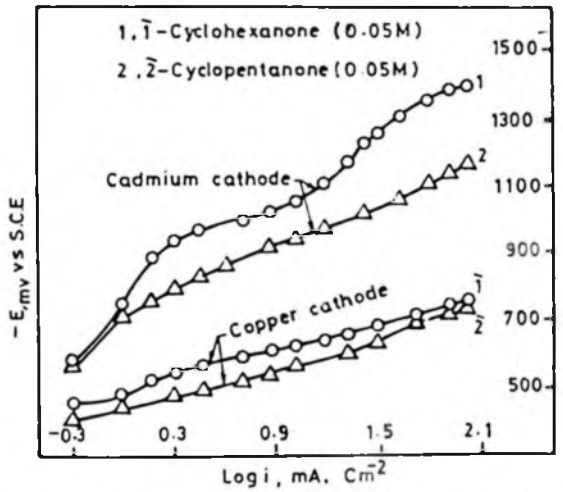


Fig. 2 The effect of cathodes material on the cathodic polarization of the two studied ketones.

TABLE 1

THE ORDER OF THE OVERALL ELECTRODE PROCESS DURING THE REDUCTION OF CYCLOHEXANONE

Cu-cathode		Cd-cathode	
E, v.	n	E, v	n
0.7	0.15	0.9	0.185
0.8	0.24	1.0	0.29
0.85	0.40	1.1	0.45

Cyclopentanone exhibits similar behaviour. The variation of n values with the potential at which reduction takes place may throw some light on the stepwise reduction of cyclohexanone. In the cathodic polarization curves (Fig. 2), a break which takes place at certain potentials depending on the nature of the cathode material was noticed. It seems that at these potentials of break, one electrode process vanishes and another one replaces it. From literature [6], it is known that the reduction of aromatic aldehydes and ketones may proceed up to alcohol formation in two steps: 1) the formation of the free radicals -C(OH) - H and 2) these radicals may participate in either coupling reaction to form the corresponding pinacol or in further cathodic reduction process to give alcohol.

The efffect of ethanol ratio in acid medium has been studied and the data obtained is recorded in Table 2. From these data it is obvious that the reducibility of cyclohexanone (0.1 M) in acid medium increases with increasing alcohol content to a certain limit

TABLE 2

THE EFFECT OF ALCOHOL CONTENT ON THE REDUCTION EFFICIENCY (F) OF CYCLOHEXANONE (0.1 M) in acid medium

% ethanol	10	20	30	40	50	60	70	80	90
C.d mA cm^{-2}	Reduction efficiency								
4	84.3	86.5	90.4	82.5	82.1	79.8	78.2	73.0	68.1
6	67.9	73.2	73.8	72.5	70.4	68.3	67.1	62.2	58.8

and start to decrease passing through a maximum (at ∽ 30% ethanol). This behaviour may be explained on the basis of the increase in solubility of some reduction products hardly soluble in water (e.g. cyclohexanol as an expected product in the present investigation). Thus the formation of cyclohexanol is inhibited in aqueous solutions making the whole reduction process more difficult which leads to lower reduction efficiences. On the other hand, the decrease of reducibility observed at higher percentage of ethanol (more than 30%) could be attributed to the blocking of cathode surface by alcohol molecules which inhibit the adsorption and consequently the reduction of the ketones.

The effect of plating current density during cadmium plating on the reducibility of the two cyclic ketones has been studied (Fig. 3). From this figure it is clear that when the current density of cadmium plating increases the current efficiency of ketone reduction increases too. But over a certain value of plating current density (i_p ∽ 10 mA.cm^{-2}), the reducibility of the ketone passed through a maximum and started to decrease. The reducibility which is assumed to proceed via their adsorption on the cathode surface is thus expected to increase by the decrease of the grain size of the metal surface (cathode). It is well known that at low current densities, the grain size of the metal deposits is coarser than that at higher currents [7]. On cathodes with coarse-grained structure, the adsorption of organic molecules is expected to be lower than on fine grained or highly dispersed surfaces [8].

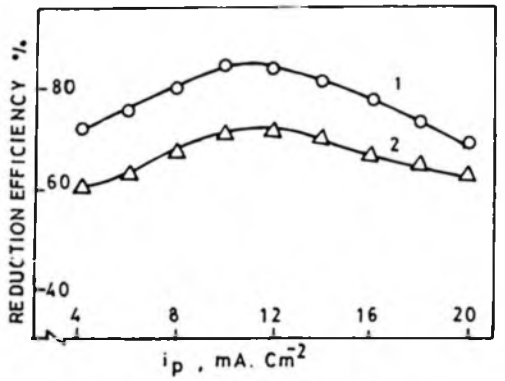


Fig. 3 The effect of plating current density of cadmium (i_p) on the reduction efficiency at 4 mAcm^{-2}.

1 Cyclohexanone (0.1 M)
2 Cyclopentanone (0.1 M)

The reducibility of the two cyclic ketones has been also studied in both neutral and alkaline media at cadmium cathode electrodeposited at 10 mA.cm^{-2}. Representative curves for cyclopentanone (0.1 M) in Fig. 4 show that the

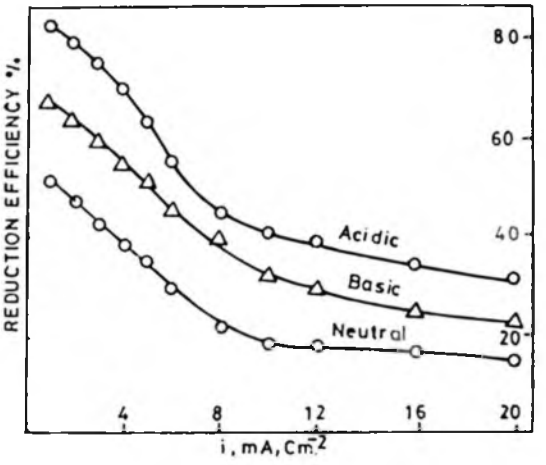


Fig. 4 Reduction efficiency of cyclopentanone (0.1M) at cadmium deposited at 10 mA cm^{-2}

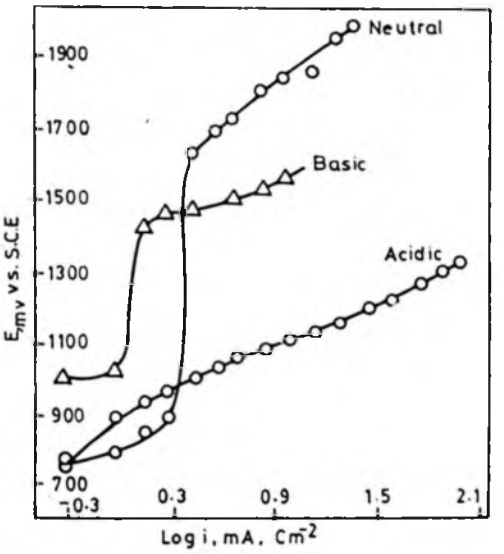


Fig. 5 The effect of different media on the cathodic polarization of cyclopentanone (0.05 M) at Cd-cathode

reducibility of cyclopentanone in acid medium is higher than that in neutral or alkaline media over a wide range of current densities. It is well known that the reduction of carbonyl compounds in alkaline medium is more difficult than in acidic medium [6]. Furthermore, the reducibility of carbonyl compounds appears to be determined by the availability of protons in the solvent on the one hand and the hydrogen overvoltage on the other [9]. In alkaline or neutral media, protonation of the carbonyl group is more difficult than in acid medium because of the low hydrogen ion concentration and accordingly, the reducibility decreases Another factor to be noted is that a more negative potential is required for further reduction in both neutral and alkaline media (Fig. 5).

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