# Electrochemical Reduction of Some Ketones

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The electrochemical reduction of acetophenone(I), 4-acetylpyridine(II) and 2-acetyl thiophene(III) in aquous ehtanol in the presence of 1.0 N $H_2SO_4$ has been investigated at copper, electrolytic cadmium and electrolytic lead cathodes. The reduction efficiency(A) is found to be higher at electrolytic cadmium and electrolytic lead cathodes than that at copper cathode. The reduction efficiency of the studied ketones can be arranged in the following order: compund III > compound I > compound II

The electroreduction of carbonyl compounds has been the subject of study of many authors(1,2). They proposed that the reduction of carbonyl functions involves the formation of free radical $R - \overset{\overset{O}{|}}{C} - R$.
OH

The acivity of carbonyl compounds towards electrochemical reduction is reported to be highly dependent on their structure(3). The effect of substituents on the reducibility of aldehyde and ketones was well studied(4,5). The activity of different cathodes towards the reduction of carbonyl compounds depends to a great extent on the nature and structure of their surfaces(6). The reduction is much enhanced on spongi like-surface metals than on smooth ones. Many authors studied the effect of metal salts addition on the reducibility of some aldehydes(7). The addition of a certain metal salt makes the reducibility of the studied aldehydes higher than that measured at electrode of this metal with no addition of its ion.

In the present work the reduction of three typical ketones at cadmium and lead cathodes is compared with reduction at copper cathode in the presence of cadmium sulfate or lead acetate over a wide range of current densities.

## EXPERIMENTAL

The electrolytic cell used for reduction consisted of two compartments separated by a porous diaphragm of sintered glass. The anode was a platinum sheet of 4.0 $cm^2$. Surface area, while the cathode was made of copper spiral of 5.0 $cm^2$ . Surface area. The electrolyte used was aqueous ethanol(1:1) containing 1.0 N $H_2SO_4$. Each cathode was pretreated chemically before every experiment and then kept in solution under investigation for about 20 minutes without polarizng current. Small concentrations of cadmium sulfate or lead acetate (0.001 M) are added to electrolytic to examine the effect of freshly deposited metal. In such case polarization was carried out for 5 minutes at 40 $ma/cm^2$ . This cathodic treatment resulted in the formation of a thin layer of metal deposit:Cadmium cathodes were made by electrodeposition on the spiral copper cathodes for 1.0 hour from the following baths(8):

| | | |
|---|---|---|
| a- Cadmium bath: | $CdSO .8/3 H_2O$ | 65 g/1. |
| | $(NH_4)_2 SO_4$ | 35 g/1. |
| | $Al_2(SO_4)_3 . 18 H_2O$ | 30 g/1. |
| | Glue | 0.7 g/1. |
| | C.d. | 1.0 $A/dm^2$ |
| b-Lead bath: | $Pb(CH_3COO)_2$ | 150 g/1. |
| | $CH_3COOH$ | 40 g/1. |
| | O-toludine | 1 ml/1. |
| | $CS_2$ | 1 ml/1. |
| | Gelatin | 1 g/1. |
| | C.d. | 1.0 $A/dm^2$. |

All chemicals used were of analar grade. They were employed without further purification.

The current efficiency of reduction(A) was measured by comparing the evolved hydrogen over the working cathode with that collected over a cathode in a cell connected in series with the working cell and containing the solvent and $H_2SO_4$ only(9). The small concentration of cadmium sulfate or lead acetate is also added to the coulometer in case of addition of these salts to the electrolytic cell.

The cathodic potentials were measured against a saturated calomel electrode. Temperature during electrolysis was kept at 30°C ± 0.1.

## RESULTS AND DISCUSSION

THE EFFECT OF CATHODE MATERIAL AND METAL SALTS ADDITIONS:

The reduction efficiency of acetophenone(I), 4-acetyl pyridine (II) and 2-acetyl thiophene(III) at metallurgical copper (in absence and presence of 0.001 M Cadmium sulfate or lead acetate),

electrolytic cadmium and electrolytic lead cathodes has been investigate. Representative curves are shown in Fig. 1 for 2-acetyl thiophene

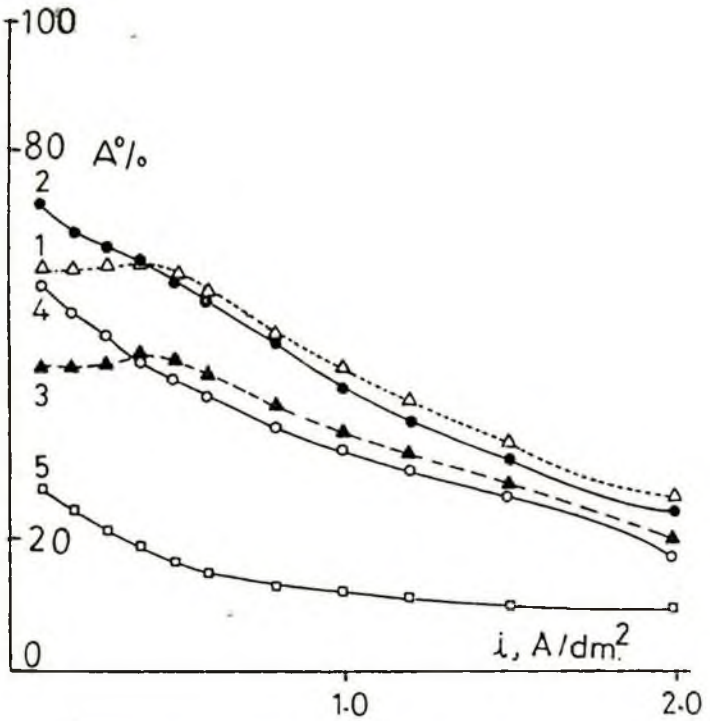



Fig. 1 The effect of cathodes material on the reduction efficiency (A) of 2-acetyl thiophene (0.05 M) at 30°C.

1. Copper cathode and 0.001 M $Cd^{2+}$ in solution.
2. Electrodeposited Cd cathode
3. Copper cathode and 0.001 M $Pb^{2+}$ in solution.
4. Electrodeposited Pb cathode.
5. Metallurgical copper cathode.

(0.05 M) reduction. From this figure, it is quite clear that the reduction efficiency of 2-acetyl thiophene at both electrolytic cadmium and electrolytic lead cathodes is higher than that at metallurgical copper cathode. This behaviour is quite common for many organic depolarizers and is attributed to the Hydrogen overvoltage variations of the cathodes. The electrolytic cadmium and electrolytic lead cathodes are known to possess high values of hydrogen overvoltage, compared to copper(10).

The reduction efficiency(A) of 2-acetyl thiophene is also markedly accelerated at copper cathode in presence of $Cd^{++}$ or $Pb^{++}$ ions relative to that in case of electrolytic cadmium or electrolytic cathodes when the current density is higher than 0.4 $A/dm^2$ The other two studied Ketones exihibited the same behaviour.

The higher reduction efficiency in the presence of metal salt (0.001 M) and at higher current density values is attributed to the formation of a very thin layer of the metal deposit on the copper cathode. This formed deposit is highly dispersed, very fine-grained and spongy film. The adsorption of organic matter on such metal films is greater than that on compact surfaces. The real surface area of spongy metal deposits is higher than the geometrical area. Using such an electrode, the real current density would be actually much less than the nominal current density hence higher 'A'. In order to confirm the role played by surface properties of the cathode, experiments were carried out for 2-acetyl thiophene reduction at electrolytic cadmium deposited at varying current densities. The results show that by increasing the current density of plating, the efficiency of reduction on the formed cathode increased (see Table 1).

**TABLE 1**

VARIATION OF REDUCTION EFFICIENCY OF 2-ACETYL THIOPHENE (0.05 M) AT CADMIUM ELECTRODE PLATED AT VARYING CURRENT DENSITIES

| C.d. of deposition $A/dm^2$ | 0.5 | 0.75 | 1.0 | 1.5 | 2.0 |
|---|---|---|---|---|---|
| Reduction efficiency (A%) | 59.0 | 61.5 | 64.0 | 69 | 72.8 |

It is well known that at low current densities of plating, the grain size of the metal deposits is coarser than at higher currents(4). On cathodes with coarse grained structure, the adsorption of organic compounds is expected to be lower than on fine-grained or highly dispersed surfaces(11). The reducibility of the studied Ketones, which is expected to proceed viz their adsorption on the cathode surface is thus expected to increase by the decrease of grain size of the cathode surface.

The low reduction efficiency observed in presence of metal salt (0.001 M) and at current density values less than 0.4 $A/dm^2$. with respect to that at electrolytic metal could be attributed to the redissolution of the thin layer formed on the copper cathode in the acidic medium.

At high values of current density and in the presence of metal salt the rate of deposition of metal is higher than the rate of dissolution of it in acid. Thus the surface is still covered by a very thin layer of metal deposit. While at low values of current density, the rate of dissolution of the formed thin layer is more than the rate of deposition and the cathode behaves as copper cathode which possess low reduction efficiency. This spongy and very thin layer is easier to dissolve than electrodeposited metal at lower

concentrations of $H_2SO_4$ in the electrolyte (0.5 N, 0.25 N and 0.1 N) to throw some light on this phenomenon. The results (Table 2) show that the reduction efficiency of the ketones is higher in presence of metal salt than on electrolytic metal at still lower values of current density with lowering $H_2SO_4$ concentration used in the electrolyte. This is in good accord with the above explanation.

**TABLE 2**

VARIATIONS OF REDUCTION EFFICIENCY OF 2-ACETYL THIOPHENE (AT 0.4 A/dm$^2$.) WITH CONCENTRATION OF $H_2SO_4$ USED IN ELECTROLYTE

| Cathode | Current efficiency(A%) in $H_2SO_4$ of | | | |
|---|---|---|---|---|
| | 1.0 N | 0.5 N | 0.25 N | 0.1 N |
| Electro-lytic Cd | 64.0 | 65.0 | 65.0 | 65.8 |
| Cu + 0.001 M Cd electrode | 63.5 | 65.0 | 70.6 | 75.5 |

From the above it is clear that it is more advantageous to use small concentration of metal salt in solution with metallurgical metal cathode.

THE EFFECT OF THE CHEMICAL STRUCTURE OF THE DEPOLARIZER:

It was found that the reduction efficiency of the studied ketones varies widely depending upon their chemical structure.

Representative curves are shown in fig.2 for the electrochemical reduction of the studied ketones (C = 0.05 M) at electrolytic cadmium cathode in acid medium. From this figure, it is quite clear that the reduction efficiency of the ketones can be arranged in the following order: 2-acetyl thiophene > acetophenone > 4-acetyl pyridine. These compounds have the same behaviour at other cathodes (Cu in the absence and the presence of metal salt and electrolytic lead).

The low reduction efficiency of 4-acetyl pyridine may be ascribed to an increase in electron density on carbonyl group. The corbonyl group of 2-acetyl thiophene also should be less active due to the presence of two lone pairs of electrons on sulfur hetero atom. However the high reduction efficiency of 2-acetyl thiophene is due to the reduction of thiophene ring itself as well as the reduction of carbonyl group. It is well known that the reduction of thiophene ring is easier than the reduction of benzene ring or pyridine

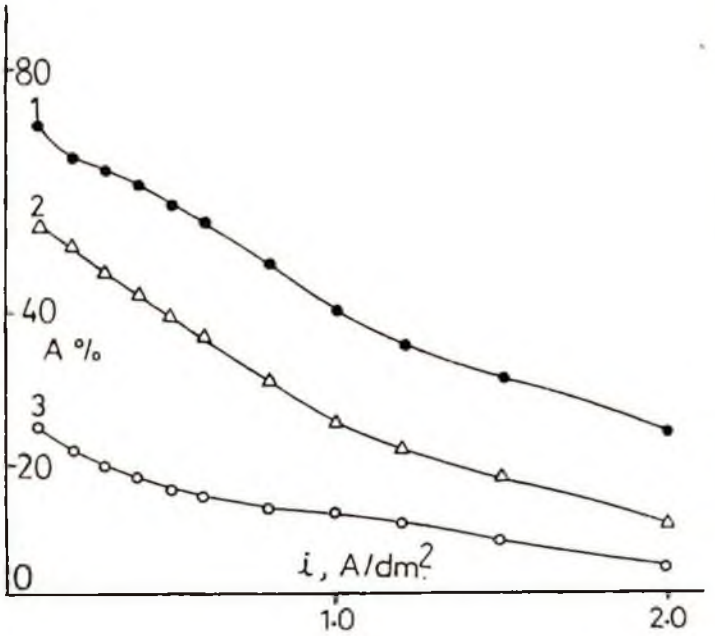



Fig. 2 The reduction efficiency (A) of the three ketones (0.05 M) at electrodeposited cadmium (deposited at 1.0 A/dm$^2$ ) and 30°

1. 2-acetyl thiphan 2. acetophenone
3. 4-acetyl pyridine

ring. The presence of two reducible functional groups give high reduction efficiency for 2-acetyl thiophene

THE CATHODIC POLARIZATION:

A representative galvanostatic polarization curves at the different cathodes for 2-acetyl thiophene are illustrated in fig.3. The reduction potentials are near the hydrogen evolution potentials on copper cathode, while at both cadmium and electrolytic lead cathodes, the hydrogen evolution process occurs at sufficiently higher cathodic potentials. This explains the low reduction efficiency at copper cathode.

From fig. 3 it is also clear that on using copper cathode in the presence of metal salt ($Cd^{++}$ or $Pb^{++}$), the reduction potentials vary widely with the variation of applied current densities. The first portion up to $i \simeq 0.4$ A/dm$^2$ . The cathode behaves like copper cathode only. The second portion at $i > 0.4$ A/dm$^2$., the cathode behaves like Cd or Pb cathodes.

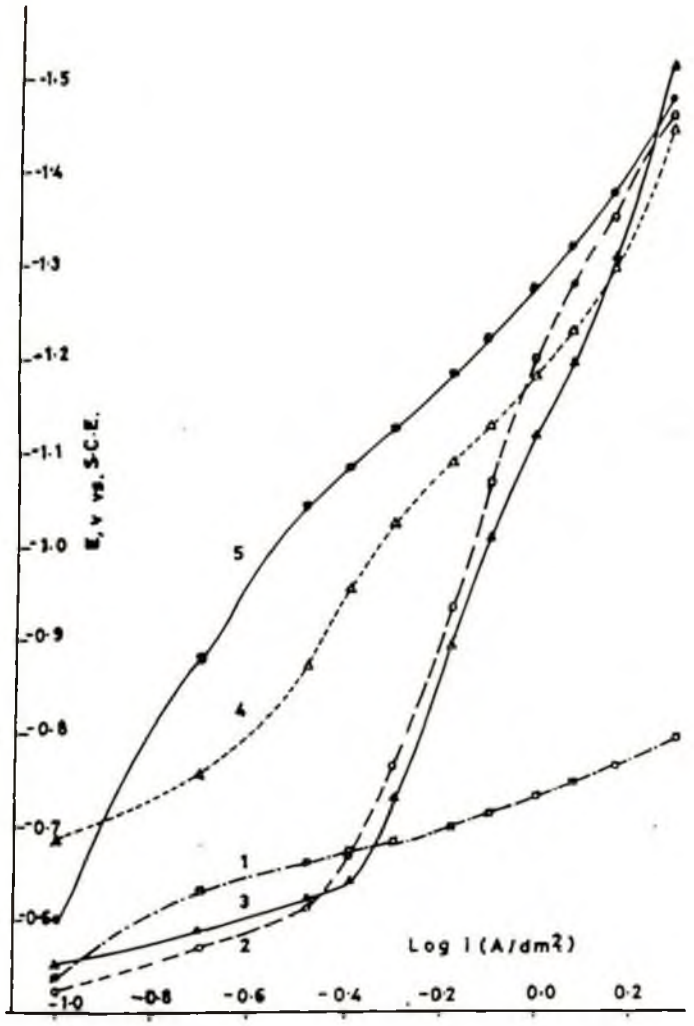



Fig. 3 The effect of cathodes material on the cathodic polarization of 2-acetyl thiophene (0.05 M) reduction at 30° C.

1. Metallurgical Cu cathode
2. Metallurgical Cu cathode with 0.001 M Pb in solution
3. Metallurgical Cu cathode with 0.001 M Cd in solution
4. Electrodeposited Cd cathode
5. Electrodeposited Pb cathode

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