Electrochemical Reduction of Some Organic Compounds Containing Carbonyl and Azomethine Groups

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Electrochemical reduction of 4-benzylidene amino-acetophenone (I), 4-benzylidene amino [Phenyl (ethanol)] (II) and p-amino acetophenone (III), is investigated in acid medium at different cathodes and at different C.D. Reduction efficiency of (I) was found to be higher than expected while (III) possesses lowest reduction efficiency.

Maironovsky et.al(1) studied the reduction of carbon-nitrogen double bond using alkali metal amalgams. The electrochemical reduction of azomethine compounds has been found to occur via electronic mechanism before protanation (2,3). The activity of carbonyl compunds towards electrochemical reduction is highly dependent on their structure(4).

The aim of the present study is to investigate the reducibility of azomethine and carbonyl in separate compounds and compare it with the reduction of a compund having both the groups in a single compound.

EXPERIMENTAL

Compounds 4-benzylidene amino acetophenone [C_6H_5- CH = N - $C_6H_4CO\ CH_3$] (I) and 4-benzylidene amino [Phenyl (ethan-2 ol)] [C_6H_5- CH = N - C_6H_4- CH (OH) - CH_3] II were prepared by condensation of benzaldehyde with the corresponding organic amine in ethanol medium in presence of a few drops of piperidine. p-Amino acetophenone [NH_2-C_6H_4- CO. CH_3] III was available. All chemicals used are of AR grade (Prolabo). Appropriate weight of the organic substance was dissolved in 1:1 ethanol containing 1.0 N H_2SO_4.

Metallurgical copper, electrodeposited cadmium or electrodeposited lead cathode are prepared(4) and used. Electrolytic cell and experimental conditions are as described (4). Current efficieiences of reduction are calculated as before.

RESULTS AND DISCUSSION

The current efficiency of reduction (A) of the investigated compounds (I II and III) was measured over a wide range of current densities at metallurgical copper, electrodeposited cadmium and electrodeposited lead cathodes. The results show that the reduction efficiency (A) decreases on increasing the applied current density for all the studied compounds. Representative curves of current efficiency vs current density at electrodeposited cadmium cathode are shown in fig.1. This behaviour could be explained as a result of the cathodic potential variations with the applied current density (see fig 2). At lower

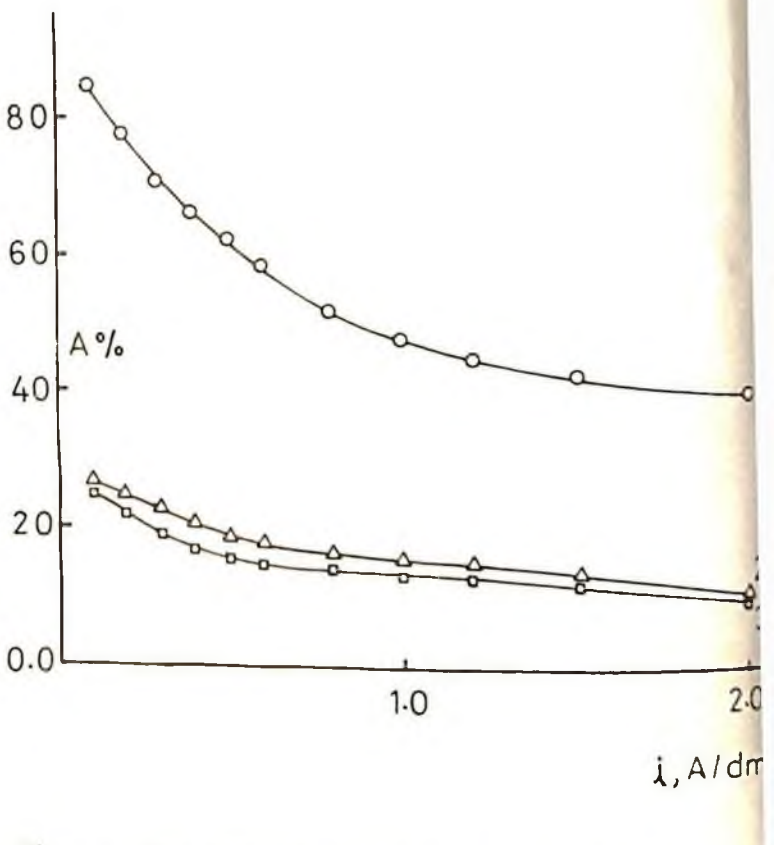


Fig. 1 The reduction efficiency (A) of the studied compounds (0.05 M) at electrolytic cadmium (performed at 0.05 M) and 30°C.

values of current, the participation of the depolariser in the cathodic process is considerable while at higher current densities, the hydrogen evolution became the main cathodic process.

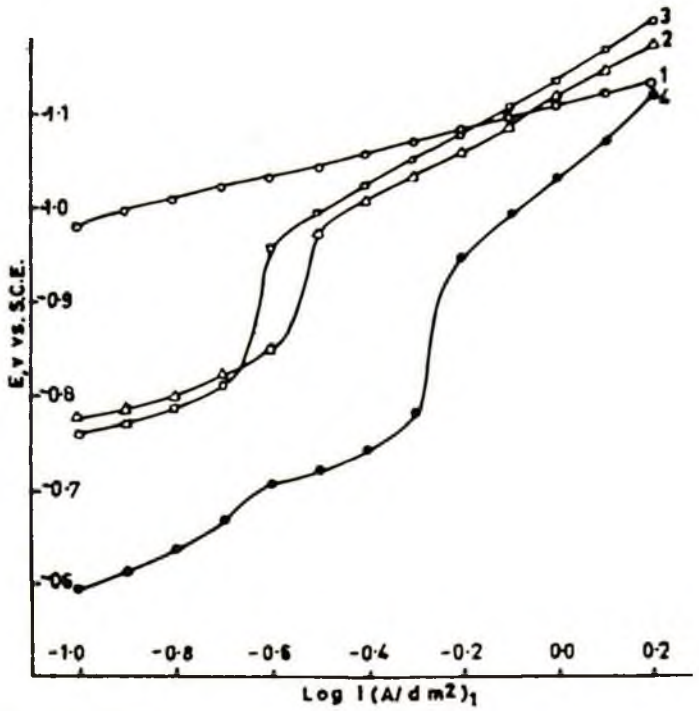


Fig. 2 The cathodic polarization curves of the studied compounds (0.05 M) at electrolytic cadmium.
curve 1 No depolarizer
curve 2 Compound II
curve 3 Compound III
curve 4 Compound I

The results showed that the reduction efficiency is higher at electrodeposited cadmium and electrodeposited lead rather than that at the metallurgical copper. Representative curves for the reduction of compound I (0.05 M) at different cathodes are shown in fig. 3. The other depolarizes exhibits similar behaviour. It is well known that cadmium and lead cathodes possess higher hydrogen overvoltage(5), Cadmium and lead electrodes are capable of separating the potentials at which the hydrogen evolves and the depolarizer is reduced. A representative galvanostatic cathodic polarization curves of the different cathodes for compound I(0.05 M) are illustrated in Fig. 4.

Compound I possesses extreamly high reduction efficiency while compound III possesses the lowest one and close to that of compound II(see fig 1). The low reducibility of compound III can be ascribed to the electron donar character of the $-NH_2$ group, resulting in increasing the electron density of carbonyl group. The high reduction efficiency of compound I with respect to compounds II and III could be attributed firstly to the presence reducible functional groups (azomethine and carbonyl). The activity of carbonyl group in compound I towards reduction is more than that in compound III and this is due to the decrease of

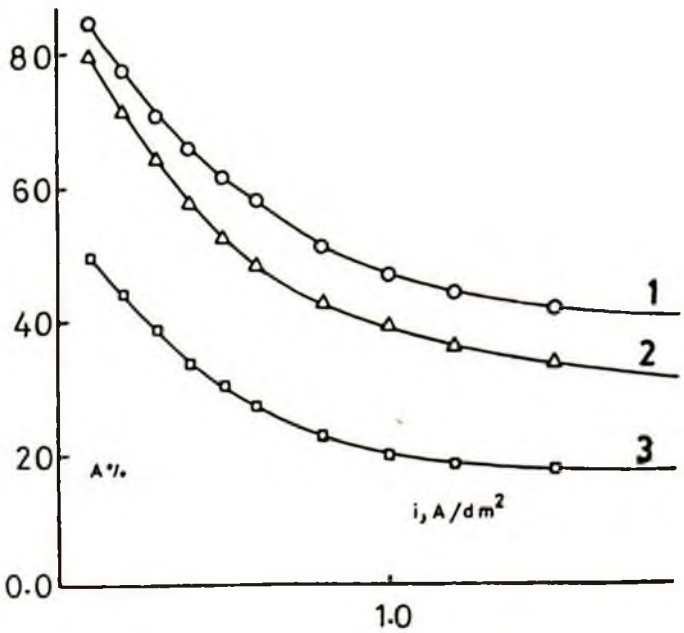


Fig. 3 The effect of cathode material on the reduction efficiency of 4-benzylidene amino acetophenone (0.05 M) at 30°C
1. Electrodeposited cadmium cathods
2. Electrodeposited lead cathode
3. Metallurgical copper cathode

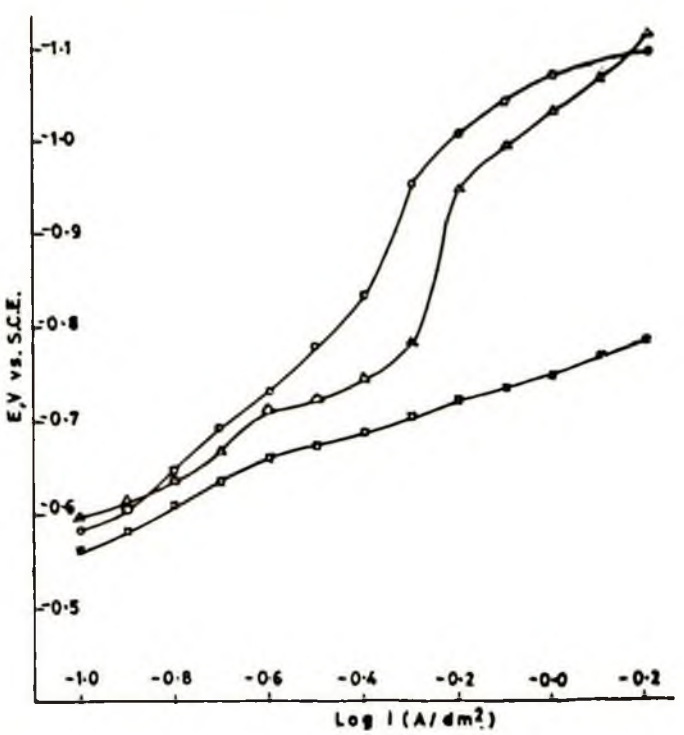


Fig. 4 Effect of cathode material on the cathodic polarization of compound I (0.05 M) reduction at 30'C
1. Electrodeposited lead Cathode
2. Electrodeposited cadmium cathode
3. Metallurgical copper cathode

electron density on carbonyl group (as a result of azomethine formation). Further the reducibility of azomethine group in compound I may be higher than that in compound II and this may be explained from the low reduction efficiency of compound II.

The relation between log i and E, (see figs.2 and 4) is found to obey Tafel's equation to a certain limit (first portion), indicating that the reduction process is kinetically controlled upto the region of the limiting current (i) where the diffusion step becomes the rate-determining step. From fig. 2 it is clear that compound I (at electrolytic Cd) exhibit two steps of reduction in polarization curves, while the other two compounds did not exhibit this phenomena. Further more, fig.2 shows that compounds II and III are reduced at the more negative potentials than compound I. This in turn confirms to our previous explanation.

REFERENCES

1. S.G. Mairanovskii, A.P. Tomilov, M. Ya. Fioshin and V.A. Smirnov, Elektrokhimiya Organic Cheskikh Socdinenii, Moscow (1968) p.547.

2. A.M. Osman, F. El-Cheikh, Z.H. Khalil and A.I. Khodair, J. Appl. Chem. Biotechnol., 26 (1976) 126.

3. F. El-Cheikh, A. Hammam, A. El-Sayed and G.A. Noubi, Bolletein of Science, Assiut University 7 No. 2 (1978).

4. Hesham Mansour, J. Electrochem Soc., India 34 (1985) 47.

5. Chemistes Handbook, III, Moscow, Khimiya (1963).

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