

THE ROLE OF CHEMICAL STRUCTURE AND THE MEDIUM IN THE REDUCIBILITY OF SOME AROMATIC ALDEHYDES

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The electrochemical reduction of benzaldehyde, salicylaldehyde and anisaldehyde were investigated at metallurgical copper and electrolytic cadmium cathodes in aqueous ethanol (1:1) containing 0.25 M H_2SO_4 . It was found that the reducibility of the studied aldehydes can be arranged in the following order: anisaldehyde > salicylaldehyde > benzaldehyde.

The influence of the medium (acidic, basic and neutral) on the reduction process has been investigated. All the studied aldehydes possess the highest reducibility in acidic medium and the lowest one in basic medium. The work was also extended to investigate the effect of the concentration of both acid and base on the reduction process. The potential measurements were carried out using galvanostatic technique. The Tafel's slope and the order of the overall electrode process in acidic medium were evaluated.

Key words: Medium effect, Aromatic aldehydes, Electrochemical reduction.

INTRODUCTION

Many authors [1-5] studied the reduction of carbonyl compounds using different cathodes. Carbonyl compounds can be reduced in one electron route to give pinacols, in two electron process to give an alcohol or finally by four electron mechanism to produce hydrocarbon [6]. The activity of carbonyl compounds towards electrochemical reduction is highly dependent on their structure and substituents [5,7,8].

In the present work we aimed to investigate the effect of the chemical structure and the reduction medium of some aromatic aldehydes.

EXPERIMENTAL

The electrolytic cell used consisted of two compartments separated by a porous diaphragm of sintered glass. The anode was a platinum sheet of 4.0 cm² surface area, and copper spiral cathode of 5.0 cm² surface area. The electrolytes were as follows:

Aqueous ethanol(1:1) + 0.25 M H_2SO_4	acidic medium
Aqueous ethanol(1:1) + 0.25 M NaOH	basic medium
Aqueous ethanol(1:1) + 0.25 M Na_2SO_4	neutral medium.

The cathode was treated chemically before every experiment and kept in solution under investigation for about 10 minutes without polarizing current. Spiral copper cathodes were electroplated with cadmium to be used as cadmium cathodes for one hour from the following bath [9]:

$CdSO_4 \cdot 8/3 H_2O$	65 g/l.
$(NH_4)_2SO_4$	35 g/l.
$Al_2(SO_4)_3 \cdot 18 H_2O$	30 g/l.
Glue	0.7 g/l.
C.d.	1.0 A/dm ²

All chemicals used were of analar grade.

The current efficiency of reduction (F) was taken as a measure for the ease of reduction of the carbonyl function:

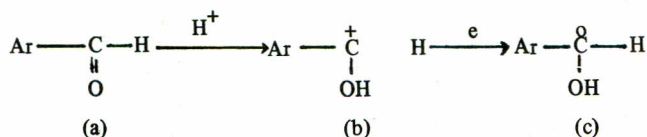
$$F = \frac{V - V'}{V} \times 100$$

where V and V' are the corrected volumes of hydrogen evolved over the coulometer and the working electrode respectively. The temperature during electrolysis was kept at $30 \pm 0.1^\circ$. The cathodic potentials were measured against a saturated calomel electrode.

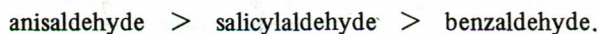
RESULTS AND DISCUSSION

In the present study the electroreduction of benzaldehyde, salicylaldehyde and anisaldehyde was investigated at metallurgical copper and electrolytic cadmium cathodes over a wide ranges of current intensity and concentration. The effect of current intensity, concentration and the nature of cathodic material on the reduction efficiency had been discussed in numerous previous publications [4,5,10,11].

The effect of the aldehydic structures. In acidic medium the reduction of aldehydes and ketones may proceed via the following mechanism:



The reducibility of the studied aldehydes in acidic is found to be in the following order :



The study was carried out on electrolytic cadmium and metallurgical copper cathodes and the obtained results are shown in Fig. 1. The high reducibility of anisaldehyde

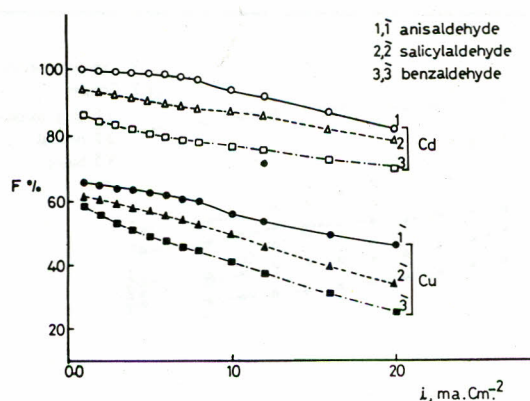


Fig. 1. Reduction efficiency of the studied aldehydes (0.1M) in acidic medium.

could be due to the methoxy group in para-position which stabilizes the formed carbonium ion and free radical (b and c). The stability of these intermediates depends on the aromaticity and the delocalization of charge density of the radical. In salicylaldehyde, the hydroxyl group also stabilizes the intermediates (free radical and carbonium ion) to some extent. The anisaldehyde intermediates are most stable, while those of benzaldehyde are the least stable ones, and reflects the reducibility of the studied aldehydes.

Polarization measurements. From the cathodic behaviour of the reduction potentials of the three studied aldehydes in acidic medium at copper and cadmium cathodes, was observed to shift towards more positive values (less cathodic) by increasing concentration. The concentration of benzaldehyde, salicylaldehyde and anisaldehyde affects the overall rate of the cathodic reduction according to the power function:

$$i(E) = KC^n$$

By plotting $\log i$ vs. $\log C$ the values of n can be evaluated (Table 1). It is obvious that the order(n) of the overall electrode process generally decreases by increasing reduction potential (Table 1). This could be ascribed to the

Table 1. The order of the overall electrode process during reduction of aldehydes at different cathodes.

Compound	Copper cathode		Cadmium cathode	
	E,V	n	E,V	n
Benzaldehyde	0.6	0.145	0.8	0.19
	0.65	0.145	0.9	0.18
	0.7	0.14	1.0	0.165
	0.8	0.115	1.1	0.155
	0.9	0.10	1.2	0.125
Salicylaldehyde	0.5	0.25	0.8	0.31
	0.55	0.22	0.9	0.3
	0.6	0.22	1.0	0.26
	0.7	0.19	1.1	0.255
Anisaldehyde	0.8	0.19	1.2	0.19
	0.5	0.24	0.75	0.35
	0.6	0.26	0.8	0.33
	0.7	0.235	0.9	0.34
	0.8	0.18	1.0	0.29
	0.9	0.19	1.1	0.265

different contribution of aldehyde reduction to the overall electrode process. At lower potentials, the reduction efficiency of the studied aldehydes is higher than that at higher potentials. The contribution of aldehyde in reduction process is greater at lower reduction potentials.

The values of Tafel's slope b_1 (at lower potentials) and b_2 (at higher potentials) are evaluated (Table 2). The variation of b values (b_1 and b_2) confirms the different nature of both cathodic processes at low and high potentials. It seems that one electrode process is being replaced

Table 2. The values of b (Tafel's constant) for the reduction of aldehydes at copper and cadmium cathodes.

Compound	Concentration, M	benzaldehyde		salicylaldehyde		anisaldehyde	
		Cu	Cd	Cu	Cd	Cu	Cd
0.1	b_1	0.10	0.135	0.13	0.165	0.145	0.215
	b_2	0.22	0.28	0.18	0.30	0.19	0.30
0.075	b_1	0.10	0.13	0.125	0.175	0.14	0.19
	b_2	0.205	0.265	0.185	0.285	0.195	0.29
0.05	b_1	0.105	0.145	0.115	0.15	0.13	0.195
	b_2	0.21	0.23	0.165	0.27	0.155	0.27
0.025	b_1	0.095	0.15	0.11	0.16	0.12	0.16
	b_2	0.19	0.225	0.145	0.255	0.155	0.275
0.01	b_1	0.09	0.15	0.10	0.16	0.95	0.145
	b_2	0.165	0.22	0.14	0.215	0.15	0.235

at relatively higher replaced at relatively higher potentials by the other.

The effect of the medium on the reduction efficiency.

The electrochemical reduction of benzaldehyde, salicylaldehyde and anisaldehyde within concentration ranges 0.01-0.1 M was carried out at metallurgical copper and electrolytic cadmium cathodes in acidic, basic and neutral media. The obtained results showed that these aldehydes possess the highest reduction efficiencies (F) in acidic medium and lowest values in basic medium at copper and cadmium cathodes. Representative curves for the reduction of anisaldehyde (0.1 M) are shown in Fig. 1. The other two studied aldehydes also exhibit similar behaviour.

The observed high reduction efficiency (F) of aldehydes in acidic medium with respect to basic and neutral media may be due to the increase of hydrogen ion concentration from basic to acidic medium encouraging the protonation of the reducible functional groups. The electrochemical reduction of carbonyl compounds appears to be controlled by the availability of protons in the solvent [12]. Our observations [2] are in confirmity with those of Elving and Leone [2], showing ease of reduction of carbonyl compounds in acid medium. The decrease of hydrogen ion concentration from acidic to basic media makes the protonation of reducible functional groups more difficult and hence decreasing the reducibility.

Representative curves for the cathodic galvanostatic polarization of anisaldehyde (0.05 M) at cadmium cathode in different media are shown in Fig. 2. The other two aldehydes behave similarly. From Fig. 2, it can be seen

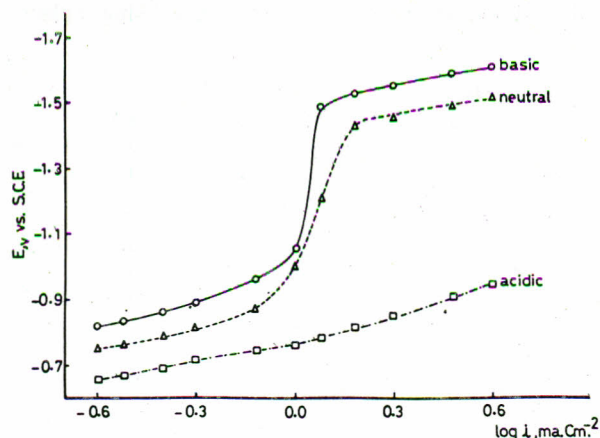


Fig. 2. The cathodic polarization curves of anisaldehyde (0.05M) in different media.

that higher negative potentials are needed for further reduction in acidic and basic media than neutral. Medium in confirmity with our explanation.

The work was also extended to investigate the effect of varying concentrations of H_2SO_4 in acid and NaOH in basic media on the reducibility of aldehydes. In acidic medium, the results (Table 3) showed that the reduction

Table 3. The effect of acid content on the reduction efficiency (F) of aldehydes (0.05 M) at 5.0 ma.cm⁻².

Compound	Reduction efficiency (F %)					
	0.25	0.5	0.75	1.0	1.25	1.5
Benzaldehyde	66.2	70.1	73.5	73.7	73.45	74.1
Salicylaldehyde	78.0	81.7	85.2	86.0	86.5	86.8
Anisaldehyde	86.4	90.5	95.0	95.5	95.2	95.1

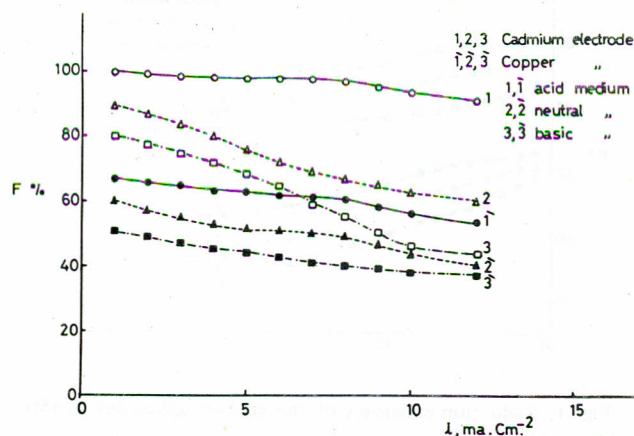


Fig. 3. Reduction efficiency of anisaldehyde (0.1M) at cadmium and copper electrodes in different media.

efficiency increases by increasing acid concentration (up to 1.0 M). Above 1.0 M the reduction efficiency was found to be independent of acid concentration. The increase in the reducibility with increasing acidity confirms the role played by protons in the reduction process. While at higher concentrations of H_2SO_4 (more than 1.0 M), the hydrogen discharge becoming easier inhibits the whole reduction process [13]. Supplemented by the decrease of the mobility of all reaction species due to increasing viscosity of the solution by increased H_2SO_4 concentration. It can therefore be concluded that the chance the reducible functions in the cathodic process (its reduction) decreases with increasing hydrogen ion concentration. On the other hand the transfer of hydrogen ion from the bulk of solution to cathodic area takes place in different ways.

In basic medium, the increase of NaOH concentration from 0.25 M to 1.5 M always leads to relative decrease in the reducibility of aldehydes (Table 4). This behaviour could be ascribed to the low hydrogen ion concentration for the necessity of a more negative potential to achieve further reduction as mentioned before.

Table 4. The effect of NaOH content on the reducibility (F) of the studied aldehydes (0.05 M) at 5 ma.cm⁻².

Base conc., M Compound	Reduction efficiency (F %)					
	0.25	0.5	0.75	1.0	1.25	1.5
Benzaldehyde	45.0	41.2	41.0	38.2	36.7	34.6
Salicylaldehyde	52.1	48.3	46.4	44.9	42.5	39.0
Anisaldehyde	60.0	59.7	54.5	53.2	51.4	48.0

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