

Electroinduced aldol condensation at platinum electrode

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Abstract : The electroinduced synthesis of aldols were carried out at controlled potential electrolysis in the neutral medium. The products are formed by the subsequent dehydration of aldols at the platinum cathode. The electrolysis was carried out at constant cathode potential in an electrolytic cell assembly containing reaction mixture, working as well as counter electrodes and a reference electrode. The products α -methylcrotonaldehyde, α -methylcinnamaldehyde, α -methyl-*p*-methoxycinnamaldehyde and α -methyl-*p*-hydroxycinnamaldehyde, formed during the electrolysis are reported here.

Keywords : Aldol condensation, platinum electrode, aldehydes.

In the present communication, we are reporting the result of our studies on electroinduced aldol condensation of some aldehydes. The species involved in the reaction are propanal (2 mole), benzaldehyde with propanal, anisaldehyde with propanal, *p*-hydroxybenzaldehyde with propanal i.e. both general and crossed aldol condensation were studied. All the electrolysis were carried out at constant potential¹⁻⁴. For the constant potential electrolysis we used conventional three electrode cell assembly with platinum working as well as counter electrode and saturated calomel electrode as reference electrode^{3,4}.

At the definite potential electrode surface is covered by coloured material, which is continually diffused in the bulk.

Results and discussion

The electroinduced synthesis of aldol in non aqueous system³ is independent on pH and takes place through free radicals²⁻⁴. The chemical aldol condensation takes place in the presence of strong base, whereas electroinduced aldol condensation does not require acidic or alkaline medium, even the subsequent dehydration, also take place in neutral medium.

Electroorganic synthesis has attracted much attention owing to several advantages such as rapid reaction rates and higher yield of pure products with non-polluting na-

ture of the reactant⁵⁻⁷.

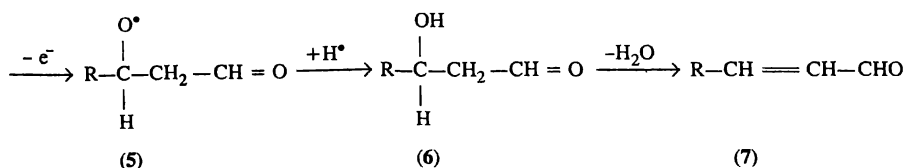
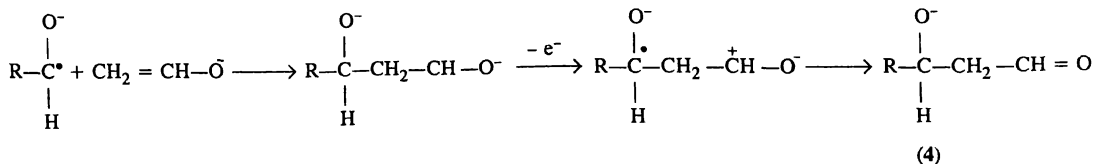
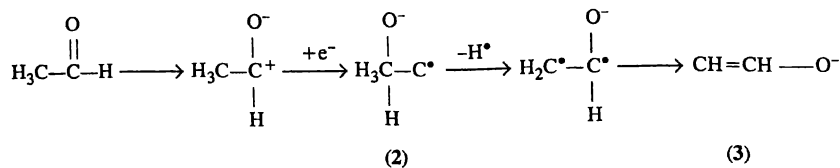
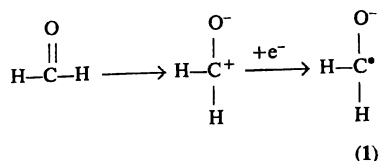
However, the mechanism of electroreduction of sulfonium and ammonium salts have been given by Shono⁸ but there is no confirmed mechanism for the electroinduced aldol condensation. For the synthesis of aldol product, we propose following mechanism which explains each step of the reaction.

In this proposed mechanism the radical anion (1) is formed from one molecule of an aldehyde by taking an electron. The molecule of other aldehyde also takes an electron to form a radical anion, which subsequently loses a hydrogen free radical to evolve an enolate anion (3). Thereafter anion (3) combines with carbon free radical (1) and by losing one electron rearranges to form anion (4). By releasing an electron (4) converts into a free radical (5) and then it combines with earlier lost hydrogen free radical to form the product aldol (6), which on subsequent dehydration forms α,β -unsaturated aldehydes (7).

In this system the reaction takes place at the room temperature in a potential range 1.55–2.20 V, but the specific potential for the reaction is found to be approximately 2.00 V.

It is evident from the Table 1 in which electrolysis were carried out at different potentials in the given range that the reaction starts at 1.55 V but the yield increases

Note



with increasing potential and we obtained the maximum yield at specific potential.

All the electrolysis were carried out at their corresponding reduction potential and were completed within one hour. After one hour no reduction product was seen to diffuse in the bulk. All the products were dark coloured liquids and entirely different from the starting aldehydes.

The observation recorded in these reaction are given in Table 1.

The product was extracted from reaction solution to

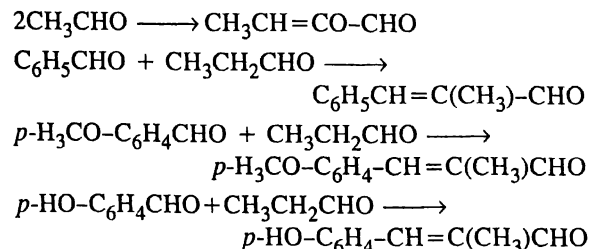
Table 1. Current-potential data of electrolysis as recorded by potential (mV) cum gavanostat

Time (h)	Current (mA)	Yield (%)
Propanal (1550 mV)		
0-1.0	0.34	>55
Benzaldehyde with propanal (1600 mV)		
0-1.0	0.34	>60
Anisaldehyde with propanal (2150 mV)		
0-1.0	0.83	>80
<i>p</i> -Hydroxybenzaldehyde with propanal (2150 mV)		
0-1.0	0.85	>80

chloroform by simple solvent extraction method after diluting reaction solution with double distilled water. The two-immiscible layers of above solvents were shaken in a separatory funnel and allowed to settle, after some time the chloroform layer containing desired product was removed.

Analysis of the products :

All the products were analyzed by chemical methods as well as by spectral studies. As per mechanism following products are obtained,



Chemical analysis :

The products were identified for unsaturation by Br₂-water test; the colour of the bromine-water decolourised rapidly on mixing with the product, which indicates the presence of unsaturation.

Spectral analysis :

IR spectra of the products show characteristic IR band at 1670 cm^{-1} corresponding to α,β -unsaturated (C=O), which was absent in the starting material.

Experimental

Reaction mixture : The reaction mixture contains the 50 mL of 0.1 M solution of starting material using dimethylformamide (DMF) as aprotic solvent + 50 mL of the 0.1 M aqueous solution of KCl, which is used as supporting electrolyte.

All the aldehydes, DMF, mercury, KCl and chloroform were of AnalaR grade. Water used was double distilled.

The electrolysis were carried out at constant potential in four necked 250 mL capacity bottle which is designed in our laboratory. For constant potential electrolysis, we have used conventional three-electrode cell assembly with platinum (flattened sheet of dimension $1\text{ cm} \times 0.5\text{ cm}$) as working as well as counter electrode. These Pt-electrodes are surrounded from one side with glass material and saturated calomel electrode (SCE) is used as reference electrode.

Conclusion :

It is evident from the studies that the electroinduced aldol formation provides a good method for electroorganic synthesis of aldol or α,β -unsaturated aldehydes and it is

a simple and ecofriendly synthetic method and hence a part of Green Chemistry.

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