Electrolytic Reduction of Aromatic Carboxylic Acids. II. Electrolytic Reduction of Cinnamic Acid(1)

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Introduction

It was reported in the previous paper(2) that the electrolytic reduction of benzoic acid at a lead cathode in acid solution gave benzyl alcohol and the reduction was favored under high pressure. Structually, cinnamic acid resembles benzoic acid, with the only exception that the latter has no α, β-unsaturated double bond between phenyl- and carboxyl-groups. It is probable, therefore, that cinnamic acid is reducible to γ-phenylpropyl alcohol under suitable conditions, as in the case of benzoic acid.

Already, Inoue(3a) reported that the electrolytic reduction of cinnamic acid at a lead cathode in alcoholic sulfuric acid solution gave the γ-phenylpropyl alcohol in 38% yield. But, later, Wilson(3b) explained that the γ-phenylpropyl alcohol and glycol which Inoue had claimed to isolate by the reduction of cinnamic acid were essentially ethyl β-phenylpropionate and diethyl β, γ-diphenyladipate respectively.

In this paper, it is intended to discuss the

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(1) This paper was presented at the Annual Meeting of the Chem. Soc. Japan, held at Tokyo, April, 1951.

(2) S. Ono and T. Yamauchi, This Bulletin, **25**, 404 (1952)

(3) a) H. Inoue, *J. Chem. Soc. Ind. Japan*, **24**, 916 (1921).
b) C. L. Wilson and K. B. Wilson, *Trans. Electrochem. Soc.*, **84**, 153 (1943); C. L. Wilson, ibid., **92**, 369 (1947).

reduction mechanism of cinnamic acid, the change in products resulting from a change in experimental conditions, and moreover, to develop the influence of external pressure in the course of the electrolytic reduction.

Experimental

(1) **Materials.**—Cinnamic acid was prepared by the usual method in this laboratory. It had a m. p. of 132-133°C. Solvents used in these experiments were ethyl-, methyl- and iso-amyl-alcohols.

Cathodes used were as follows;

a) Lead cathode: commercial products (99.9% purity), a sheet or tube type (100 cm.^{2}), it was oxidized before use.

b) Mercury cathode: purified by washing with nitric acid and distillation in a vaccum, cathode area (16 cm.^{2}).

c) Zinc amalgum cathode: prepared by the electrolytic method.(4) cathode area (16 cm.^{2}).

d) Platinized-platinum cathode: cylindrical platinum plate (100 cm.^{2}) was platinized by the electrolysis of platinic chloride solution.

(2) **Reduction Method.**—The usual diaphragm type of the electrolytic cell was used. A porous cup (17 cm. × 4.6 cm.) was placed in the cell as a cathode compartment and the cell was immersed in a water-bath to maintain the desired temperature. The reduction was carried out in the same manner as described in the previous paper.(2) Usually twice the theoretical amount of current was passed.

(3) **Isolation and Estimation of Products.**—(a) **Reduction at a Pb-, Hg-, and Hg-Zn-Cathodes.**—When the reduction was completed, the catholyte was decanted into a beaker, cooled and any precipitates which remained were filtered off. Then it was extracted with ether and washed with water.

After evaporation of ether, the remaining viscous liquid was steam-distilled.

(i) Distillate from steam-distillation was extracted with ether, and dried with anhydrous sodium sulfate. Evaporation of ether gave a liquid, which was distilled under diminished pressure. The fraction coming over at 106-112°/10 mm.Hg was collected. Redistillation gave a liquid, b. p. 110-112°/10 mm.Hg, D_4^{25} 1.0101, n_D^{25} 1.4920, identified as an ethyl β-phenylpropionate. (Found: C, 74.23; H, 7.8. Calculated for $C_{11}H_{14}O_2$: C, 74.16; H, 7.86). Saponification with 20% alcoholic potassium hydroxide solution gave a β-phenyl-propionic acid, m. p. 48-49°C.

(ii) Residual solution from steam-distillation was neutralized with potassium hydroxide solution, then extracted with a large volume of ether. Evaporation of ether gave a light yellow oily liquid from which a fine precipitate (m. p. 112-113°C.) was separated by standing overnight. Recrystallization from ethyl alcohol gave a colorless prism, m. p. 116-116.5°C. It was identified as a meso-diethyl diphenyladipate. (Found: C, 73.38; H, 7.04. Calculated for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39).

The remaining oily liquid was treated with excess potassium hydroxide solution and cooled. Acidification with conc. hydrochloric acid produced a semi-solid materials which was treated with ether. The bulk of meso-diphenyladipic acid, (m. p. 260-265°C.), remained undissolved by ether. Evaporation of ether left a highly viscous liquid, from which insoluble diphenyladipic acid (m. p. 165-170°C.), was separated by treating with hot benzene.

(b) **Reduction at a Pt-Pt Cathode.**—After completing the reduction, the catholyte was diluted with water to some extent, then extracted with ether. The ether extracts were collected, washed with water and dried over anhydrous sodium sulfate. After evaporation of ether, the remaining liquid was distilled under diminished pressure. The fractions obtained were characterized. The reduction of cinnamic acid gave a cyclohexylpropionic acid, b. p. 143-145°/11 mm. Hg., m. p. 16°C., D_4^{20} 0.9966, n_D^{20} 1.4658. (Found: C, 70.03; H, 9.68. Calculated for $C_9H_{16}O_2$: C, 69.3; H, 10.25)

(4) **Constants of Products.**—The following products were obtained in the present experiments.

(i) β-Phenylpropionic acid, m. p. 48-49°C., recrystallized from ligroin.

Ethyl ester, b. p. 110-112°/10 mm.Hg, D_4^{25} 1.0101, n_D^{25} 1.4920

Methyl ester, b. p. 126-128°/25 mm.Hg, D_4^{25} 1.0420, n_D^{25} 1.5102

iso-Amyl ester, b. p. 136-138°/7 mm.Hg, n_D^{25} 1.4840

(ii) β,γ-Diphenyladipic acid

a) Meso acid, m. p. 260-265°C, recrystallized from EtOH.

Diethyl ester, m. p. 116-116,5°C.

Dimethyl ester, m. p. 175-176°C.

Di-iso-amyl ester, m. p. 120-121°C.

b) Racemic acid, m. p. 170-175°C.

(iii) Cyclohexylpropionic acid, m. p. 16°C, b. p. 143-145°/11 mm.Hg D_4^{20} 0.9966, n_D^{20} 1.4658.

Ethyl ester, b. p. 91-94°/8 mm.Hg, D_4^{20} 0.9674, n_D^{20} 1.4488.

Results and Discussions

(1) **Effect of Cathodes.**—The reduction at a Pb cathode gave β-phenylpropionic acid (I) in 45-70%, β,γ-diphenyladipic acid (II) in 10-20% and polymeric material (III) (so-called benzene soluble factor), but Hg cathode gave only 6-10% of (I), the remaining 90% consisting of approximately equal amounts of (II) and (III). Hg-Zn cathode also gave the similar results obtained from a Hg cathode in a weak acid solution, but gave less β,γ-

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(4) Sakurai, This Bulletin, 7, 155 (1932).

diphenyladipic acid and (III) in a strong acid solution.

On the other hand, Pt-Pt cathode gave no bimolecular compounds, whereas it gave rise to cyclohexyl compounds as well as β-phenylpropionic acid. It was also determined that the reduction of unsaturated ethylenic double bond took place first and then that of benzene ring in the case of Pt-Pt cathode.

When cinnamic acid (0.05 mol.) was reduced for 6.0 amp. hrs., the main product was β-phenylpropionic acid, but the prolongation of the reduction for 15.0 amp. hrs., gave the cyclohexylpropionic acid. This fact shows that the reduction process at a Pt-Pt cathode contrast sharply with that pursued at a Pb or a Hg cathode. In any case, the carboxyl group in cinnamic acid was observed to be quite resistant to the electrolytic reduction, that is, no γ-phenylpropyl alcohol was produced.

Table 1 gives the yield of products obtained from the different type of cathodes.

The characteristic properties of the Pt-Pt cathode had been discussed in an other paper.(5)

Table 1

Effect of Cathodes

Catholyte; Cinnamic acid 14, 8 g., EtOH 60 ml., Sulfuric acid 40 ml., Quantity of Current; 12 amp. hrs., Temp. 25-35°C.

Run No.	Cathode	H_2SO_4 (%)	C. D. (amp./dm^2.)	Products. A (%)	B (%)	C (%)
1	Pb	75	3.0	70	10	
2	〃	28	3.0	45	18	
3	Hg-Zn	75	10.0	40	24	
4	〃	28	10.0	15	49	
5	Hg	75	10.0	10	24	
6	〃	28	10.0	5.7	44	
7	Pt-Pt	75	5.0		—	75
8	〃	28	5.0		—	70

Run Nos. 7 and 8; Cinnamic acid, 7.4 g., Q. of Current, 15.0 amp. hrs.

Product; A: β-Phenylpropionic acid.
B: β,γ-Diphenyladipic acid.
C: Cyclohexylpropionic acid.

Note: In the forthcoming Tables, the yield of benzene soluble factor was omitted, owing to the difficulty of separating a pure form from benzene solution in which usually small amounts of β-phenylpropionic acid and β,γ-diphenyladipic acid were included.

(2) **Effect of High Pressure.**—The special study was undertaken to develop the effect of high pressure of hydrogen in the course of electrolytic reduction. Examination of these results (Table 2 and 3), shows that the reduction of cinnamic acid under high pressure of hydrogen at a Pb, Hg, or a Hg-Zn cathode, and also at a Pt-Pt cathode, gave quite the same products as in the case of the ordinary state.

It was observed that the formation of β,γ-diphenyladipic acid was favored at high pressures, especially in the case of Pb cathode. However, an increase in the hydrogen pressure has no clear effect on the products, and moreover, at a Hg cathode, there are no remarkable changes in the yield of products.

In the case of Pt-Pt cathode, an increase in the yield of cyclohexyl compounds is not proportional to the hydrogen pressure.

So far as the hydrogen overvoltage is concerned, there would be no definite conclusion in regard to the high pressure.(6) Therefore, the influence of hydrogen overvoltage may be omitted in this stage. It is a new attempt to study the influence of high pressure in the course of electrolytic reduction of organic compounds. And the electrode reaction is not well settled for the time being; therefore, no conclusion comes from these results on this matter.

(3) **Effect of Temperature.**—In the present experiments, using either Pb, Hg, or Hg-Zn cathode, cinnamic acid gave bimolecular compounds, as well as β-phenylpropionic acid. Wilson(3b) suggested that the bimolecular compounds were produced by the dimerization of free radicals, $\mathrm{Ph\dot{C}HCH_2COOH}$, from cinnamic acid.

In connection with the acid concentration, the temperature was observed to affect the formation of bimolecular compounds.

The results are shown in the Table 4.

(4) **Reduction Mechanism.**—As for the formation of γ-phenylpropyl alcohol, cinnamic acid has a conjugated system between the phenyl and carboxyl groups, if it were probable, the reduction would proceed in the formation of β-phenylpropion aldehyde or cinnamyl aldehyde and further γ-phenylpropyl alcohol. But it must be pointed out that the carbon-double bond is more active for the electrolytic reduction, as is seen in the case of α,β-unsaturated ketones.(7)

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(5) S. Ono, T. Hayashi and J. Nakaya, Presented at the Symposium on Electro-organic Chemistry of the American Electrochem. Soc., held at Detroit, Oct., 1951.

(6) J. O'm Bockris, *Chem. Rev.*, **43**, 538 (1948).

(7) Pasternack R. and V. Halban H., *Helv. chim. Acta.*, **31**, 753 (1948).

Table 2

Effect of Hydrogen Pressure (a) Reduction at a Pb, Hg-Zn or Hg Cathode.
Catholyte; the same as in Table 1

Run No.	Cathode	H_2SO_4 (%)	Temp. (°C)	C. D. (amp./dm.^{2})	Press. (atm.)	Products A (%)	Products B (%)
1	Pb	75	50—55	10.0	—	79	6
2	〃	〃	〃	〃	25	64	14
3	〃	40	30—35	3.0	—	60	17
4	〃	〃	〃	〃	35	50	22
5	〃	〃	〃	〃	40	52	20
6	〃	〃	40—45	10.0	40	40	20
7	〃	28	25—35	3.0	—	42	20
8	〃	〃	〃	〃	25	37	28
9	〃	〃	〃	〃	45	32	36
10	〃	〃	40—45	10.0	20	32	35
11	Hg-Zn	75	40—45	10.0	—	53	18
12	〃	〃	〃	〃	20	47	22
13	〃	40	40—45	〃	—	50	22
14	〃	〃	〃	〃	20	46	28
15	Hg	75	25—30	10.0	—	12	24
16	〃	〃	〃	〃	20	12	25
17	〃	〃	〃	〃	40	11	25
18	〃	28	〃	〃	—	5.7	44
19	〃	〃	〃	〃	30	6	44

Table 3

Effect of Hydrogen Pressure (b)
Reduction at a Pt-Pt cathode

Catholyte; Cinnamic acid 7.4 g., EtOH 60 ml., Sulfuric acid 20 ml., Quantity of Current; 15 amp. hrs., Cathode (100 cm.^{2})

Run No.	H_2SO_4 (%)	Temp. (°C)	C. D. (amp./dm.^{2})	Press. (atm.)	Product. C. (%)
1	75	25—35	5.0	—	75
2	〃	〃	〃	30	76
3	40	40—45	5.0	35	75
4	〃	〃	〃	45	71
5	28	25—35	3.0	—	60
6	〃	〃	〃	20	63
7	〃	〃	〃	30	69
8	〃	〃	5.0	45	73
9	〃	〃	〃	50	73

C; Cyclohexylpropionic acid.

Table 4

Effect of Temperature
Catholyte; the same as in Table 1

Run No.	Cathode	H_2SO_4 (%)	Temp. (°C)	C. D. (amp./dm.^{2})	Products A (%)	Products B (%)
1	Pb	75	25—35	3.0	70	10
2	〃	〃	55—60	3.0	75	8
3	〃	〃	〃	10.0	79	6
4	〃	40	25—35	3.0	60	17
5	〃	〃	55—60	3.0	70	15
6	〃	〃	25—35	10.0	62	15
7	〃	28	25—35	3.0	42	18
8	〃	〃	55—60	3.0	50	15
9	Hg-Zn	75	20—25	10.0	40	25
10	〃	〃	40—45	10.0	55	12
11	Hg	40	25—30	10.0	10	38
12	〃	〃	55—60	10.0	15	35

Assuming that the reduction would take place by the following process, (shown in Fig. 1)

After coordination of proton at an alpha carbon atom, forming the free radicals and further β-phenylpropionic acid, or bimolecular compounds, there would be no conjugation between carboxyl and phenyl groups; that is, under these conditions, the electronic interaction between them no longer exists.

Therefore, the carboxyl group in cinnamic acid would not be reduced to the corresponding aldehyde or alcohol.

It is of interest to see the fact that the reduction of cinnamic acid at a Pt-Pt cathode gave cyclohexyl compounds.

Judging from the fact that (1) both α,β-unsaturated double bond and benzene ring

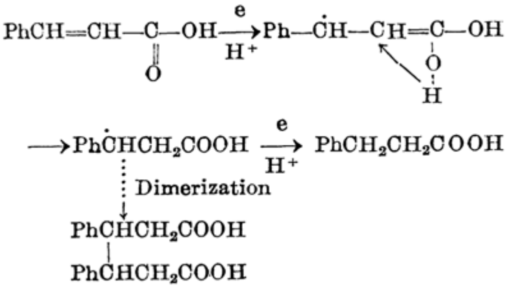

Fig. 1.—Reduction mechanism of cinnamic acid at Pb, Hg or Hg-Zn cathode.

were hydrogenated and (2) no bimolecular compounds were obtained in the case of Pt-Pt cathode, it is likely that the reduction at a Pt-Pt cathode consists mainly in the catalytic mechanism similar to the catalytic hydrogenation.

Summary

The electrolytic reduction of cinnamic acid at a Pb, a Hg, a Hg-Zn or a Pt-Pt cathode in acid solution was studied.

It was found that the formation of bimolecular compounds depended on the nature of cathode materials and the condition of the reduction. It was confirmed that the γ-phenylpropyl alcohol could not be produced by the electrolytic reduction of cinnamic acid. It was found that the reduction of cinnamic acid at a Pt-Pt cathode gave cyclohexyl propionic acid.

The effect of high pressure of hydrogen in the course of reduction was discussed.

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