Electrolytic Reduction of Aromatic Carboxylic Acids III. Reduction of Phenylacetic Acid(1)

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In the previous papers we reported that the electrolytic reduction of benzoic acid(2) at a Pb cathode gave a benzyl alcohol. On the other hand, the reduction of cinnamic acid(3) at a Pb or a Hg cathode gave no γ-phenylpropyl alcohol but gave rise to bimolecular compounds as well as β-phenylpropionic acid.

Already Inoue(4) reported that the reduction of phenylacetic acid with a Pb cathode in the alcoholic acid solution gave a β-phenylethyl alcohol (53.4%) and a small amount of phenylpinacone. Marie(5) also reported that the carboxyl group in phenylacetic acid could be reduced to alcohol (33%), but gave no pinacone. The result of the former is different from the latter.

In this paper, it is intended to discuss the reduction of phenylacetic acid in relation to the results obtained from both benzoic- and cinnamic-acids, especially in regard to the formation of the alcohol from carboxylic acid. Another object of this study is to investigate the effect of platinized platinum cathode (Pt-Pt) in the course of the electrolytic reduction.

Experimental

(1) Materials.—Phenylacetic acid was a commercial product, and further purified by recrystallization. It had a m. p. of 76°C. Cathodes used were the same materials as in the case of previous paper.(3)

(2) Reduction Method.—The reduction, including the case of high pressure of hydrogen, was carried out in the same manner as described in the previous paper.(3) In the case of Pb, Hg and Hg-Zn cathodes, usually three times the theoretical amount of current was used.

(3) Isolation and Estimation of Products.— **(i) Reduction at Pb-, Hg- and Hg-Zn cathodes** When the reduction was completed, the catholyte was diluted with water, and then extracted with ether. After the evaporation of the ether, the remaining liquid was steam-distilled.

The distillate from steam-distillation was extracted again with ether. The ether solution was dried with anhydrous sodium sulfate. After the vaporization of the ether, an oily liquid was obtained. The liquid contained ethyl phenylacetate, phenylethyl alcohol and small amounts of phenylethyl phenylacetate, and the latter was distilled under diminished pressure, b. p. 110~116°/7 mm.Hg., m. p. 29°C. The oily liquid was saponified with 20% alcoholic potassium hydroxide solution, and extracted with ether. The ether solution was dried with anhydrous sodium sulfate. After the vaporization of the ether, the colorless fragrant oil was fractionated at 98~102°/11 mm.Hg. The fraction has d_4^{20} 1.0325 and n_D^{20} 1.5217 (Found: C, 78.15; H, 8.10. Calculated for $C_6H_5CH_2CH_2OH$: C, 78.68; H, 8.19%). Thus it can be regarded as phenylethyl alcohol.

The residual solution from steam-distillation was neutrallized with potassium hydroxide, and then extracted with ether. The evaporation of the ether gave a small amount oily liquid from which no pinacone compound was obtained.

(ii) Reduction at a Pt-Pt Cathode. After completing the reduction, the catholyte was diluted with water, and extracted with ether, and then dried over anhydrous sodium sulfate. After the vaporization of the ether, the remaining liquid was distilled under diminished pressure. The two fractions, (f_1) 65~80°/6 mm.Hg and (f_2) 114~119°/6 mm.Hg were obtained.

Redistillation of (f_1) gave a liquid, b. p. 68~70°/6 mmHg. d_4^{25} 0.9475, n_D^{25} 1.4472. The fraction (f_1) was saponified with 20% alcoholic potassium hydroxide solution, and extracted with ether. The ether solution was dried with anhydrous sodium sulfate. After the vaporization of the ether, the residual liquid was distilled under diminished pressure. The fraction has 117~119°/6 mm.Hg, d_4^{25} 0.9953, n_D^{25} 1.4590 (Found: C, 67.52; H, 9.79. Calculated for $C_6H_{11}CH_2COOH$: C, 67.60; H, 9.86%). Thus the fraction (f_1) can be regarded as ethyl cyclohexylacetate.

The fraction (f_2) was distilled again under diminished pressure, and gave a liquid, b. p. 117~119°/6 mmHg, d_4^{22} 0.9955, n_D^{22} 1.4588 (Found: C, 67.73; H, 9.78. Calculated for $C_6H_{11}CH_2COOH$: C, 67.60; H, 9.86%). Thus it can be regarded as cyclohexylacetic acid.

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(1) This paper was presented at the regular meeting of the Chemical Society of Japan, held at kyoto, on May, 1951.

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

(3) S. Ono and T. Hayashi; ibid. **26**, 11 (1953).

(4) H. Inoue; *J. Soc. Chem. Ind. Japan*, **24**, 914 (1921).

(5) M. Marie; *Bull. Soc. Chim.*, **25**, 512 (1919)

Results and Discussions

(1) Formation of Phenylethyl alcohol.—The optimum conditions for the preparation of phenylethyl alcohol from phenylacetic acid at a Pb cathode are shown in the Table 1.

Table 1

Optimum conditions for the formation of phenylethyl alcohol

Investigator	$PhCH_2$-COOH (g.)	EtOH (cc.)	H_2SO_4 (%) (g.)	Current quantity (A. hrs.)	Yield (%)
Marie(5)	20	20	50 50	40	33
Inoue(4)	20	20	75 70	40	53.4
Authors	13.6	40	50 50	30	28
〃	13.6	40*	50 50	30	35.3

Current density: 10 amp/dm.² Temp: 60°C.

*, Cellosolve was used as a solvent instead of EtOH.

It is a well-known fact that the ester compound is not suitable for the preparation of the corresponding alcohol by the electrolytic reduction, as is seen in the case of benzoic acid.(6) Comparing the results of Table 1, it is surprizing that Inoue's condition gave the yield higher of alcohol, even though his condition seems to be more likely to give the ethyl phenylacetate than those of other's.

In the present experiment, it was found that the cellosolve is available as a solvent to avoid the formation of ester compound.

We have found that the electrolytic reduction of the carboxyl group is most easily possible when it is directly attached to an aromatic ring in a series of carboxylic acid, such as benzoic acid. In the case of phenylacetic acid, the carboxyl group is isolated by the CH_2-linkage from the phenyl group; therefore, it is expected that the electronic interaction between phenyl and carboxyl groups would be less effective than in the case of benzoic acid. That is, the yield of alcohol from phenylacetic acid is smaller than that from benzoic acid. Cinnamic acid or phenylpropionic acid gave no γ-phenylpropyl alcohol as stated in the previous paper.(3) It may be expected that the relative ease of the reduction of carboxyl group is closely related to the nature of R-groups. (R=Ph-, $PhCH_2$- or $PhCH_2CH_2$-)

(2) Effect of Cathode.—In the present experiment, lead (Pb), zinc amalgam (Hg-Zn), mercury (Hg) and platinized-platinum (Pt-Pt) cathodes were used in order to determine the effect of cathode materials on the reduction products. Pb, Hg-Zn and Hg cathodes were observed to act analogously, giving the phenylethyl alcohol.

We have found that Pb cathode is preferable to Hg-Zn or Hg cathode, for the formation of phenylethyl alcohol.

On the other hand, the reduction at a Pt-Pt cathode gave rise to cyclohexyl compounds and it seemed that the behavior of the Pt-Pt cathode was quite the same as in the case of benzoic-and cinnamic-acids.(7)

(3) Effect of Solvents.—(i) **Reduction at a Pb Cathode** When sulfuric acid and ethanol are used as a catholyte, we have found that the 50% of sulfuric acid solution is available for the formation of phenylethyl alcohol. In the case of high concentration of sulfuric acid solution, the yield of phenylethyl alcohol is decreased by the formation of ethyl phenylacetate which will be less reactive for the formation of phenylethyl alcohol. We have studied that when 75% of sulfuric acid and ethanol are used as a catholyte, more than 60% of phenylacetic acid is esterified without using the current at 60°C.

To avoid the esterification, ethyl acetate and cellosolve were used as a solvent, and the later gave the better yield. Results are shown in the Table 2.

Table 2

Effect of Solvents

Catholyte: Phenylacetic acid 13.6 g, Sulfuric acid 40 cc., Solvent 40 cc. Current density: 10 amp/dm.² Current quantity: 30 A·hrs. Cathode: Lead (1.0 dm.²)

Run No.	Solvent	Temp. (°C.)	Phenylethyl alcohol (%)
1	MeOH	50	25.0
2	EtOH	60	28.0
3	$CH_3COOC_2H_5$	60	29.0
4	$C_2H_5OCH_2CH_2OH$	60	35.3

Table 3

Effect of Acid concentration

Catholyte: Phenylacetic acid 13.6 g, EtOH 40 cc., Sulfuric acid 40 cc. Cathode: Pt-Pt sheet (1 dm.²). Current quantity: 28 A. hrs. (Theor. 16.1 A. hrs.). Temperature: 30∼35°C.

Conc. of H_2SO_4%	C. D. amp/dm.²	product f_1 (g.)		product f_2 (g.)		Yield f_2(Total)* (%)	C. E. (%)
		(g.)	(%)	(g.)	(%)		
28	2	6.0	35.3	6.0	42.3	79.4	45.7
50	2	9.5	55.9	3.0	21.1	77.9	44.8
75	2	10.5	61.8	1.5	10.6	72.8	41.9

Products: f_1; Ethyl cyclohexylacetate.
f_2; Cyclohexylacetic acid.

* Sum of f_2 and cyclohexylacetic acid produced from the hydrolysis of f_1.

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(6) (a) For example, Swann, *Trans. Electrochem. Soc.* **75**, 411 (1939), and reference (2).

(b) S. Ono and J. Nakaya reported at the regular meeting of the Chemical Society of Japan held at Tokyo, April, 1951. that the electrolytic reduction of ethyl phenylacetate at Pb cathode gave no phenylethyl alcohol.

(7) c. f. Part I and II of this series, ref. (2) and (3).

(ii) **Reduction at a Pt-Pt Cathode** It was seen from the data in the table 3 that the yield of ethyl cyclohexylacetate was increased and the yield of cyclohexylacetic acid was decreased with the increase of the acid concentration. In the same acid concentration, it was found that better yields could be obtained at a lower current density (Table 4).

Table 4
Effect of Current Density

Catholyte: Phenylacetic acid 13.6 g, EtOH 40 cc., 50 % sulfuric acid 40 cc. Cathode: Pt-Pt sheet (1 $dm.^2$). Current quantity: 28 A. hrs. (Theor. 16.1 A. hrs.). Temperature: 30∼35°C.

C. D. ($amp/dm.^2$)	Yield (%)	C. E. (%)
0.5	81.5	46.9
1.0	80.2	46.1
2.0	76.5	44.0
3.0	74.6	42.9
4.0	75.5	43.4
5.0	75.5	43.4

Product; Cyclohexylacetic acid.

(4) **Effect of High Pressure.**—In a series of this investigation, the special study was made in order to know the effect of external pressure in the course of electrolytic reduction of phenylacetic acid.

Table 5
Effect of high pressure
(a) Reduction of Phenylacetic acid at a Pb Cathode

Catholyte: Phenylacetic acid 13.6 g., Sulfuric acid 40 cc., Cellosolve 40 cc. Cathode: Lead sheet (1 $dm.^2$). Current quantity: 30 A. hrs. (Theor. 10.7 A. hrs.). Temperature: 50∼55°C.

H_2SO_4 (%)	C. D. ($amp/dm.^2$)	Press. of H_2 (atm.)	Yield (%)	C. E. (%)
50	5.0	—	33.0	11.7
〃	〃	25	32.5	11.6
〃	〃	35	33.8	12.0
75	5.0	—	25.5	9.1
〃	〃	40	26.4	9.4
〃	10.0	40	32.4	11.5
28	5.0	—	30.3	10.8
〃	〃	20	31.5	11.2
〃	10.0	40	32.8	11.7

Product: Phenylethyl alcohol.

The reduction was undertaken at the high pressure of hydrogen (15∼40 atm.). In the case of the reduction at a lead cathode, the product was quite the same as the ordinary pressure. Results are given in the Table 5. Among these data, a slight increase in the product was observed at the high pressure, but an increase of the hydrogen pressure made no clear effect on the product. If, in the case of Pt-Pt cathode, we may assume that the reduction consists mainly in the catalytic mechanism, it can be expected that there is some correlation between the reduction products and the external pressure. But we have fairly comparable data in this experiment; (Table 6), therefore, further studies must be made to clarify this problem.

Table 6
Effect of high pressure
(b) Reduction of phenylacetic acid at Pt-Pt Cathode.

The electrolytic conditions are the same as tab'e 4, except the external pressure of hydrogen.

C. D. (amp/dm^2)	Press. of H_2 (atm.)	Yield (%)	C. E. (%)
3·0	—	74.6	42.9
〃	15	75.5	43.4
〃	30	76.0	43.7
4.0	25	76.8	44.2
〃	35	76.0	43.7
5.0	25	78.2	45.0
〃	40	79.0	45.4

Product: Cyclohexylacetic acid.

Summary

(1) The electrolytic reduction of phenylacetic acid at a Pb, a Hg-Zn, a Hg or a Pt-Pt cathode was studied. It was confirmed that phenylethyl alcohol could be produced from phenylacetic acid using Pb, Hg-Zn and Hg cathodes. The Pt-Pt cathode was observed to behave catalitically in the course of reduction and gave rise to cyclohexylacetic acid.

(2) The relative ease of the reduction of the carboxylic acid to alcohol was closely related to the nature of the group which lies between phenyl and carboxyl radical.

(3) The effect of high pressure of hydrogen was discussed on the electrolytic reduction of phenylacetic acid.

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