Electrolytic Reduction of Aromatic Carboxylic Acids. I. Reduction of Benzoic Acid under Pressure⁽¹⁾

By Shin-ichi ONO and Tsuneo YAMAUCHI

(Received May 7, 1952)

A number of investigations have been carried out on the electrolytic reduction of benzoic acid, but all of them were made at ordinary pressure in an open vessel. The authors, therefore, studied this problem under the pressure of hydrogen and carbon dioxide to find out the effect of the pressure on the reduction products.

(1) Reduction of Benzoic Acid to Benzylalcohol.—C. Mettler(2), Fr. Fichter and Israel Stein,(3) H. Inoue,(4) Sherlock Swann and G. D. Lucker,(5) studied this problem in the alcoholic sulfuric acid solution by using a lead cathode with good yields. The authors carried out electrolysis in alcoholic sulfuric acid solution by using a lead cathode and compared the yield of benzyl-alcohol obtained under the various pressures of hydrogen and carbon dioxide with that obtained in an open

---

(1) Presented at the annual meeting of the Chem. Soc. of Japan in 1950.

(2) C. Mettler, *Ber.*, **38**, 1745 (1905).

(3) Fr. Fichter, Israel Stein, *Helv. Chim. Acta.*, **12**, 821 (1929).

(4) H. Inoue, *J. Soc. Chem. Ind. Japan*, **24**, 806 (1921).

(5) Sherlock Swann and G. D. Lucker, *Trans. Electrochem. Soc.*, **75**, 411 (1939).

vessel. Not only hydrogen but also carbon dioxide had an important effect on the yield of the reduction product. The yield increased in proportion to the pressures of hydrogen or carbon dioxide respectively. (Table 1)

(2) **Reduction of Benzoic Acid to Benzaldehyde.** — Hugo Weil(6) and Mettler(7) studied this problem by using a mercury cathode and benzene, and obtained benzaldehyde with 30—50% yield. Benzaldehyde was removed to a benzene layer from a water layer and protected from reduction to alcohol.

S. Tesh. Alexander Low(8) obtained 50% benzaldehyde by using sodium bisulfite which combined with benzaldehyde instead of benzene, but only 20% by Mettler's method.

The authors carried out the electrolysis by using a mercury cathode in a mixture of boric acid, sodium sulfate solution and benzene. The yield increased in accordance with the pressure of hydrogen. In case of carbon dioxide the yield decreased as the pressure increased. (Table 2)

(3) **Reduction of Benzoic Acid to Ethyl Hexahydrobenzoate.**—Emill Müller(9) electrolysed benzoic acid in alcoholic sulfuric acid solution by using a lead cathode, and obtained a hydro-compound, but F. Somlb(10) identified this to be dihydro benzoic acid ethylester. Fr. Fichter(11) obtained benzylalcohol mainly by the same method, and predicted that one will obtain hydro-compound when the current density is small.

The authors carried out the electrolysis in alcoholic sulfuric acid solution by using a platinized platinum cathode. When the pressure of hydrogen or carbon dioxide was increased, the yield of ethylhexahydrobenzoate decreased but the yield of hexahydrobenzoic acid increased.

It was thought that ethyl benzoate was formed from benzoic acid under this condition and the ester was reduced to ethyl hexahydrobenzoate.

It was found that the electrolytic reduction of benzoic acid at a platinized platinum cathode in alcoholic sulfuric acid solution gave rise to hexahydrobenzoic acid and its ester, but no benzylalcohol.

These results contrast sharply with that obtained from a lead cathode. It was assumed that there would be an essential difference between the nature of lead and platinized platinum cathode in the course of reduction.

Examination of the Table 4 shows that the hydrogen pressure has an effect on the reduction products.

Experimental

(1) **Reduction of Benzoic acid to Benzylalcohol.**—The electrolytic conditions were as follows: cathode: lead plate, 1 dm.^{2}; cathodic solution: 10 g. of benzoic acid, 70 g. of sulfuric acid, 60 g. of ethyl alcohol; anode: lead; anodic solution: 30% sulfuric acid; current density: 5 amp./dm.^{2}; Temperature: 30—50°C.; current quantity: 10 amp. hrs.; Pressure: 1—30 atmosphere.

The temperature was kept under 50°C. by using a water bath and by stirring the cathodic solution vigorously; the current was passed until 10 amp. hrs. were reached.

When the electrolytic reduction was completed, the catholyte was poured into water and extracted with ether. The ether solution was dried with anhydrous sodium sulphate. After the vapourization of the ether, the pale yellow fragrant oil was fractionated at 180—220°C. The fraction was saponified with 2N caustic soda and was extracted with ether and distilled. The fraction between 196—203°C. has specific gravity of 1.045 at 20°C. and refractive index $n_D^{25}=1.5283$ (those of benzylalcohol are $D^{15}=1.0507$, $n_D^{25}=1.53866$ respectively). It dissolved calcium chloride and gave the odour of benzaldehyde when warmed with nitric acid. Thus we regarded this fraction as benzylalcohol. When the residual water solution at the above mentioned extraction was acidified by adding sulfuric acid, the precipitation was gained. This was identified as benzoic acid, judging from its freezing point. Hydrobenzoin and benzene were not detected.

To study the effect of pressure, the electrolytic cell with a stirrer was placed in an autoclave specially designed* for this purpose. The gas was introduced to remove the air, and then the desired pressure was maintained and a series of electrolytic reductions was made under pressures of 1—30 atmosphere.

Result are summerized in Table 1.

Table 1

Pressure of H_2	Yield		Current Efficiency
1 atm.	4.5 g.	50.8%	44.6%
10	5.6	63.2	55.4
15	6.5	73.4	64.4
30	7.2	81.3	71.4
Pressure of CO_2	Yield		Current Efficiency
1 atm.	4.5 g.	50.8%	44.6%
10	5.0	56.4	49.5
20	5.2	58.7	51.5
30	5.5	62.1	54.5

---

(6) Hugo Weil, D. R. P. 196, 293 (1906).

(7) C. Mettler, *Ber.*, **41**, 4148 (1906).

(8) Alexander Low, *Tran. Am. Elec. Chem. Soc*, **45**, (1924).

(9) E. Baur and E. Müller, *Zeit. Elektrochem.*, **34**, 98 (1928).

(10) F. Somlb, *Zeit. Elektrochem.*, **35**, 264 (1929).

(11) Fr. Fichter, *Helv. Chim, Acta.*, **12**, 821 (1929).

* S. Ono, *J. Chem. Soc. Japan*, **73**, 852 (1952).

(2) Reduction of Benzoic Acid to Benzaldehyde.—The electrolytic conditions were as follows: cathode: mercury (16.2 cm.^{2}); cathodic solution: 6.5 g. of sodium sulphate, 6.5 g. of boric acid, and 5 g. of sodium benzoate were dissolved into 85 cc. of water and 50 cc. of benzene for fixation of the aldehyde added to this solution.

anode: lead; anodic solution: 10% aquous solution of sodium sulphate; current density: 6 amp./dm.^{2}; current quantity: 4 amp. hrs.; temperature: 20—25°C.; presure: 1—30 atm.

After breaking the current, we continued the stirring further on for about one hour to utilize the reducing power of sodium amalgam. Then the catholyte was separated from mercury and 100 cc. of 10% sulfuric acid was added and steamdistilled. The distillate was extracted with ether and the ether solution was neutralized with sodium bicarbonate to remove the unreduced benzoic acid to the water layer.

The ether solution was dried with anhydrous sodium sulphate. After stripping the ether, we gained benzaldehyde with boiling point 179°C. The water solution was acidified and the precipitated benzoic acid was recovered. On the contrary, aldehyde was not obtained in the case of lead-, platinized platinum-, or copper-cathode. This reason is explained as follows: Mercury acts as sodium amalgam by which benzoic acid is reduced to aldehyde, and then sodium amalgam turns back to mercury. In this case, the system of the mercury and sodium amalgam was circulated by electrolysis. Thus the yield of aldehyde was increased by keeping the experimental conditions to suit the formation of sodium amalgam. If the catholyte became alkaline, the velocity of the action of sodium amalgam on benzoic acid was slowed down. On the contrary, by maintaining it in a condition to make the above-said velocity speedy, the formation of sodium amalgam was decreased.

When the electrolytic reduction was undertaken at high pressure of hydrogen atmosphere, the yield of aldehyde was increased with the pressure, but in the carbon dioxide atmosphere the yield was decreased with the increase of the pressure. The latter can be illustrated as follows: the increase of the amount of carbon dioxide dissolved in catholyte decomposes sodium benzoate to benzoic acid and the catholyte increases acidity, so that the yield decreases. It seems that the dissolution of carbondioxide and benzoic acid in benzene makes the dissolution of aldehyde in benzene more difficult.

Results are summarized in Table 2.

Table 2

Pressure of H_2	Yield		Current Efficiency
1 atm.	0.6 g.	16.3%	7.6%
20	1.1	29.9	13.9
30	1.6	43.3	20.1
Pressure of CO_2	Yield		Current Efficiency
1 atm.	0.6 g.	16.3%	7.6%
10	0.3	8.2	3.8
20	trace	—	—

(3) Reduction of Benzoic Acid to Ethyl Hexahydrobenzoate.—The electrolytic conditions were as follows: cathode: platinized platinum (84.2 cm.^{2}); cathodic solution: 10 g. of benzoic acid, 120 cc. of 95% alcohol, 30 g. of sulfuric acid; anode: lead; anodic solution: 30% sulfuric acid; current density: 0.5—1.0 amp./dm.^{2}; temperature: 20—30°C.; current quantity: 15—20 amp. hrs.; pressure: 1—30 atm. After electrolysis, the catholyte was filtered and the greater part of solvent was taken off under reduced pressure. The results of fractional distillation of 20 g. products are shown in Table 3.

Table 3

	fraction	yield	D_4^{25}	n_D^{25}
(1)	185—195°	5 g. (25%)	0.9506	1.4373
(2)	195—200°	9 (45)	0.9525	1.4396
(3)	200—225°	4 (20)	1.0500	1.4525
(4)	225—240°	1.6 (8)	—	—

The fraction (2) which is a colorless liquid ought to be ethyl hexahydrobenzoate from its physical constant and the hydrolysis of the fraction (2) produced hexahydrobenzoic acid. The fraction (3) seemed to be the mixture of hexahydrobenzoic acid and its ethyl ester from its physical constant. Saponification of (3) with 20% alcoholic potassium hydroxide, gave a hexahydrobenzoic acid, M. P. 28°C. The fraction (4) a greater portion of which was distilled at 233—237°C., seemed to be hexahydrobenzoic acid, but we could not confirm it as its amount was too small.

The relation between the amounts of four fractions and the pressure is shown in Table 4.

Table 4

Press. atm. / Fraction	1(H_2)	5(H_2)	10 (H_2)	30 (H_2)	10 (CO_2)	20 (CO_2)
(1) 185—195°	25%	25%	20%	23%	30%	25%
(2) 195—200°	45	40	35	23	30	25
(3) 200—225°	20	20	28	35	25	30
(4) 225—240°	8	10	12	17	10	15

In the case of the electrolytic reduction under pressure, the fraction (2), that is the ethyl hexahydrobenzoate was decreased and the fraction (3), (4) that is the mixture of ethyl hexahydrobenzoate and its acid was increased with the increase of the pressure of hydrogen. When ethyl benzoate is catalytically reduced, either hexahydro-compound or benzyl alcohol is obtained according to the catalyst. In the case of the electrolytic reduction of benzoic acid (benzoic ester) using a platinized-platinum cathode, the authors obtained ethyl hexahydrobenzoate and its acid but no benzylalcohol with small current density at ordinary or high pressures. But the yields of the reduction products differ according to the pressure.

Summary

The authors studied the electrolytic reduction of benzoic acid and compared the yield of the reduction product obtained under various pressures of hydrogen and carbon dioxide with that obtained in an open vessel. The effect of pressure in the course of electrolytic reduction was discussed and it was found that the reduction product differed according to the pressure.

The authors express their gratitude to Dr. N. Sugiyama, Professor of the Tokyo University of Education and Dr. B. Sakurai, professor of the Shinshu University for their kind advice. The expense of this work has been defrayed from the Grant in Aid for Scientific Research from the Ministry of Education, to which the authors' thanks are due.

Department of Chemistry, Faculty of Engineering,
Naniwa University, Osaka