On the Electrolytic Reduction of Aldehydes, Part V. Cinnamic Aldehyde

By

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(Received December 19, 1928)

The electrolytic reduction of cinnamic aldehyde was tried by Law[1] who reported that the aldehyde undergoes reduction neither in an acid nor in an alkaline solution, but changes to a resinous substance. By using a neutral solution, however, he succeeded in obtaining phenyl propyl alcohol with 55% yield. As the neutral catholyte he took a mixture[2] of water, alcohol, ethyl acetate and potassium acetate, in which ethyl acetate plays the part of using up alkali as it is formed. T. Shimamoto[3] also undertook to reduce the aldehyde in a sulphuric acid solution as well as in a neutral solution using platinum, lead or mercury as the cathode. The results obtained by him were always unsatisfactory, the yield of phenyl propyl alcohol having been not more than 10% even in the neutral solution. As I had, by using a sodium bicarbonate solution as the catholyte, succeeded in reducing oxybenzaldehydes[4], vanillin and piperonal[5] with the good yields of 80—90%, it was now attempted to see whether the same catholyte would not be similarly effective in the reduction of cinnamic aldehyde. When an electrode having a great over-voltage like mercury was used in a neutral catholyte the reduction of the double bond and of the aldehyde group took place simultaneously, and phenyl propyl alcohol was produced with the yield of more than 70%. Electrodes with

1 Jour. Chem. Soc., **89**, 1512 (1906); **99**, 1113 (1911); **101**, 1016 (1912).
2 Elbs, Ber., **38**, 4012 (1905).
3 The work is not yet published.
4 These Memoirs, **11**,. 407 (1928).
5 Ibid, **11**, 419 (1928).

a smaller over-voltage, such as platinum, nickel and copper only resinized the aldehyde, no corrresponding alcohol being formed. I also traced Law's experiment with a neutral solution and found the yield of phenyl propyl alcohol to be far lower than Law stated, when lead was used as the cathode. The yield was increased to 50% by substituting mercury for lead as the cathode.

In the reduction of vanillin and piperonal[1] it was observed that their reduction to the corresponding alcohols is rather hindered when alcohol is taken as their solvent, while in the case of cinnamic aldehyde the presence of a suitable quantity of alcohol in the cathode solution favours the reduction, though its excess has the contrary effect.

Experimental

1. Electrolytic Reduction in a Sodium Bicarbonate Solution

The apparatus used for the experiment was similar to that previously employed for the reduction of oxyaldehydes[2]. As the cathode solution, a saturated sodium bicarbonate solution mixed with some dilute alcohol was taken and into this solution a current of carbon dioxide was passed constantly during the electrolysis. Five grams of cinnamic aldehyde used for each experiment, were added drop by drop to the cathode solution, which was always vigorously agitated. Mercury was used as the cathode and a platinum plate as the anode. The latter was dipped in the anode solution consisting of 5% caustic soda solution.

After the electrolysis was over the cathode solution was diluted with much water and extracted with ether. The residue after evaporating the ether from the ether extract was subjected to steam distillation, and the distillate was treated with sodium bisulphite in order to fix the aldehyde remaining unchanged. Phenyl propyl alcohol was now extracted with ether, dehydrated and purified by distillation. It is a thick colourless liquid having an agreeable odour. Its boiling point was found to be 235° at ordinary pressure, 120° by 12 mm and 115° at 8 mm pressure.

0.1003 g substance: 0.2914 g CO_2 and 0.0794 g H_2O,
C=79.25%, H=8.86%; Calc. C=79.35%, H=8.89%

A residue having a gummy consistency was obtained after steam distillation. It was soluble in ether and did not crystallize even when left to

1 Loc. cit.
2 Loc. cit.

stand for several months.

The results of electrolysis under different conditions are shown in the following table.

Table I

No.	Temperature	Catholyte cc		Current density	Current quantity	Phenyl propyl alcohol	Residue
		Alcohol	Bicarbonate sol.	amp/100 sq. cm.	amp-hour	%	%
1	25°–28°	—	100	10.0	4.0	16	8
2	20°–25°	30	80	7.5	14.0	56	20
3	20°–22°	40	60	7.5	12.0	60	20
4	25°–30°	40	60	7.5	13.5	56	24
5	10°–15°	50	50	6.0	11.5	42	20
6	20°–25°	50	50	6.0	10.0	58	22
7	25°–28°	70	50	10.0	4.0	38	22
8	25°–30°	70	50	18.0	8.0	36	52
9	25°–27°	70	50	9.0	8.0	42	34
10	18°–22°	70	50	5.0	7.0	44	46
11	15°–18°	70	50	4.0	8.0	40	46
12	20°–22°	70	50	6.0	12.0	72	14
13	27°–30°	70	50	7.5	12.0	68	16
14	25°–30°	70	30	7.5	10.0	50	36

When the results shown in No. 1 and No. 7 are compared it is cleary seen that the addition of alcohol to the cathode solution greatly favours the reduction though its presence in amounts of more than 60% acts contrarily by accelerating the polymerization of the aldehyde (compare with No. 14). Both high temperature and great current density tend to increase polymerization; perhaps the temperature of 15°–20° and current density of 5—10 amperes per 100 sp. cm. are the most favourable. In the experiments from No. 7. to No. 11, 5 grams of the aldehyde were added to the cathode solution at the commencement of the reaction all at once, and as a natural consequence of this the formation of the resinous matter was greatly increased. In order to prepare phenyl propyl alcohol with a good yield it is very important to add the aldehyde drop by drop at such a rate that the second portion drops in after the first portion

has undergone reduction.

2. Electrolytic Reduction in an Alcoholic Ethyl Acetate Solution

Cathode solution : 20 cc. of ethyl acetate + 20 cc. of alcohol + 20 cc. of water + 4 gr. of potassium acetate + 5 gr of cinnamic aldehyde.
Current density : 6 amp./100 sq. cm.
Anode : Platinum plate
Anode solution : 5 % caustic potash solution

As the cathode, well purified lead or mercury was used, and the cathode solution was strongly stirred. With the cathode of lead the yield of phenyl propyl alcohol could not be raised to more than 24 %, while with the mercury cathode a 50% yield was procured.

Table II

No.	Cathode	Temperature	Current quantity amp.-hour	Phenyl propyl alcohol %	Resinous matter %
1	Pb	20°—22°	6	24	54
2	Hg	20°—22°	6	48	34
3	Hg	25°—30°	8	50	36

The electrolysis was also conducted in the cathode solution chiefly consisting of 60% acetic acid with different cathodes, but in no case phenyl propyl alcohol was produced.

In conclusion, the writer wishes to express his sincere thanks to Professor M. Matsui for his kind guidance and encouragement throughout this research.