On the Electrolytic Reduction of Aldehydes. Part III.

Ortho- and Para- Oxybenzaldehydes

By

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Ortho-Oxybenzaldehyde.

Regarding the electrolytic reduction of o-oxybenzaldehyde, or salicylaldehyde, there are found in the literature only two papers by Law and Schepps. Law¹ tried his electrolytic reduction of aldehydes by using an alcoholic sulphuric acid solution as catholyte with copper as cathode and although he generally succeeded in reducing them to alcohol and hydrobenzoin as principal products, yet with salicylaldehyde he reports that the entire substance was changed to a resinous substance.

Schepps² carried out his electrolytic reduction of the aldehydes in alcoholic sulphuric acid solution with cadmium as cathode. Although he generally succeeded in getting a tolerably good yield of the corresponding hydrocarbons, yet with salicylaldehyde he reports, in confirmation of Law's results, that o-cresol was not obtained, and the greater part of the material was converted into a resinous substance.

From these results it has been found unsuitable to use as the electrolytic solution for the reduction of salicylaldehyde so strong a mineral acid as sulphuric acid. Presumably in this case salicylaldehyde forms at

I J. Chem. Soc., 91, 754 (1907).

² Ber., 46, 2564 (1913).

first oxybenzyl alcohol, or saligenin, and this latter substance is easily polymerised by the mineral acid into such a substance as saliretin.

When, in the catholyte, an alkali is used, instead of sulphuric acid, most of the aldehydes are changed principally to hydrobenzoin, and, according to Law¹, the carbonyl compounds, first reacting with alkali, form an intermediate product as shown in the following equation

$$\mathbf{X} - \mathbf{CO} - \mathbf{Y} + \mathbf{N}\mathbf{a}\mathbf{OH} = \mathbf{X} - \mathbf{C} - \mathbf{ON}\mathbf{a}$$

and this latter product is then reduced to form hydrobenzoin as follows:

$$\begin{array}{c} \text{OH} & \text{OH OH} \\ {}_{2} \mathbf{X} - \overset{l}{\mathbf{C}} - \text{ONa} + {}_{2} \mathbf{H} = \mathbf{X} - \overset{l}{\mathbf{C}} - \overset{l}{\mathbf{C}} - \mathbf{X} + {}_{2} \text{NaOH} \\ \overset{l}{\mathbf{Y}} & \overset{l}{\mathbf{Y}} \overset{l}{\mathbf{Y}} \overset{l}{\mathbf{Y}} \end{array}$$

With salicylaldehyde, Law obtained, by using nickel or platinum plate as cathode, oxylydrobenzoin with a yield of 70 per cent:

$$_{2}$$
 OH \cdot C₆H₄ \cdot CHO + $_{2}$ H = HO \cdot C₂H₄ \cdot CHOH \cdot CHOH \cdot C₆H₄ \cdot OH

Moreover, at the same time as the above, there is produced 9-10dioxyphenanthrene.

With the purpose of preparing o-oxybenzyl alcohol by the electrolytic reduction of salicylaldehyde, I first made experiments with an alkaline solution as the catholyte. As nickel and platinum cathodes had already been tried by Law, besides those I also used copper, lead, zinc, and mercury, which have a greater over-voltage, as cathodes. With each of these no alcohol was obtained, the chief product consisting of oxyhydrobenzoin with a yield of 70 to 80 per cent. The reduction efficiency was small with platinum and nickel which have a small over-voltage, and it was greater in proportion to the rise of the over-voltage as with mercury zinc, and lead.

As I had learned from the above experiments, that for preparing o-oxybenzyl alcohol by electrolytic reduction of salicylaldehyde a strong mineral acid or a free alkali cannot be used, I performed the reduction

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¹ Law, J. Chem. Soc., 89, 1512 (1906); Kaulmann, Z. Elek. Chem., 2, 365 (1895); Elbs and Brand, Z. Elek. Chem., 8, 784 (1992).

with the electrolytic solution constantly kept only weakly alkaline by using as catholyte a solution of sodium bicarbonate into which a stream of carbon dioxide was kept passing throughout the electrolytic process for the purpose of neutralizing the free alkali as it formed. Thereupon, quite to my expectation, no resinous substance or condensation product such as hydrobenzoin was formed, and salicyl alcohol was produced with current and material yields of 80 to 90 per cent:

 $OH \cdot C_6H_4 \cdot CHO + _2H = OH \cdot C_6H_4 \cdot CH_2OH$

Moreover, when such a very weakly acid solution as sodium acetate solution acidified with acetic acid is used in place of the sodium bicarbonate solution, the yield of salicyl alcohol was found to be just as good.

Although each of the metals, mercury, zinc, copper, lead, and nickel, forms alcohol when used as cathode, the current efficiency is highest with mercury and decreases regularly with the decrease of over-voltage in the order of zinc, lead, copper, and nickel.

Experimental.

When zinc, lead, copper, and nickel were used as cathodes, the electrode was inserted into the cell and the solution was vigorously stirred



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during the electrolysis. When mercury was employed as cathode the outside of the cell was used as the cathode compartment, and a specially constructed cell having double walls served as the anode compartment. The stirrer was made to rotate in the centre of the cell as is shown in figure 1. By this device, not only a small volume of the cathode solution suffices for the purpose, and it can be easily and vigorously agitated, but also the process of reduction can be watched from outside.

J. Experiment with an alkaline solution.

Catholyte :	100 cc. of a 5% sodium hydroxide solution with 5 gr.
	of salicylaldehyde.
Anode :	Lead.
Anolyte :	5% sodium hydroxide solution.
Temperature :	16°
Current density :	1.5 amp./100 sq. cm.

The volumes of hydrogen evolved at the cathode and at the coulometer were compared and the reduction efficiency of different cathodes was estimated by the usual method. This result is shown in figure 2 which shows that the efficiency is large in proportion to the amount of the over-voltage, and that in the case of zinc it gives a value closely approximating the theoretical. On the contrary, nickel with its slight over-voltage is found to cause no reduction at all under the same conditions.

Zinc		Lead	Lead amalgam		Lead	Copper		
Time (mins.)	Reduction efficiency (%)	Time (mins.)	Reduction efficiency (%)	Time (mins.)	Reduction cfficiency (%)	Time (mins.)	Reduction efficiency (%)	
4	100.0	2	9 2. 6	2	93.4	2	82.7	
15	97.2	20	91.6	15	91.9	10	73.7	
25	95.5	40	86.3	25	91,0	20	65.3	
35	94.6	50	85.3	37	88.8	40	69,4	
48	90.0	60	79 .2	45	84.t	50	55.8	
55	81.2	70	72.3	55	78.2	65	53.8	
65	66.8	80	65.6	67	54.6	75	50.4	
74	56.1	- 90	69.2	75	23.0	- 90	42.5	
85	44.8	100	52.9	85	11.3	100	37.4	

Table I.

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The efficiency curve for zinc and lead first shows a sudden fall after the passage of electricity of one ampere-hour which is just the quantity of current required for converting salicylaldehyde into oxyhydrobenzoin. Still, the fact that the reduction does not cease at this point but that hydrogen continues to be absorbed indicates that a portion of the oxyhydrobenzoin is further reduced.



The catholyte was treated, under cooling, with about 5 gr. of hydrogen sodium carbonate and then neutralized with dilute acetic acid to the acid degree of carbonic acid.

This was done to avoid the danger of changing the precipitate formed into a dark brown substance by an acidity stronger than that of carbonic acid. The precipitate thus obtained is oxyhydrobenzoin or a mixture of its isomers, and forms a white amorphous mass which is filtered by the aid of suction, and well washed with water. It is with difficulty soluble in water, and, although soluble in alcohol and ether, does not crystallize out from these solutions. It was, therefore, dissolved in a dilute sodium hydroxide solution and then precipitated with acetic acid and thoroughly washed. About 2 gr. of the purified product were thus obtained.

The product soluble in the carbonic acid solution was repeatedly extracted with ether and subjected, after dispelling the ether, to steam distillation. On cooling the distillate there appeared some white needle crystals insolube in alkali. When recrystallized from alcohol, the substance melted at 112° (according to Law 113°) and gave on analysis the following result :

Substance, 0.1065 gr. $CO_2 = 0.3117$ gr. $H_2O = 0.0502$ gr. C = 79.75% H = 5.27%Substance, 0.0931 gr. $CO_2 = 0.2742$ gr. $H_2O = 0.0466$ gr. C = 80.34% H = 5.60%Calculated for $C_{14}H_{12}O_2$, C = 79.21% H = 5.71%

The substance is, therefore, 9–10–dioxyphenanthrene formed by the reduction of oxyhydrobenzoin as indicated in the following equation :

$$OH \cdot C_6H_4 \cdot CHOH \cdot CHOH \cdot C_6H_4 \cdot OH + 2H = \bigcirc + 2H_2O$$

The residue after steam distillation was twice extacted with ether, and the extract dehydrated with anhydrous sodium sulphate. After dispelling the ether, the resinous residue obtained was allowed to stand for one or two days, when it crystallized out in small wart like masses. This substance is soluble in alcohol, ether, and warm water. When decolorized with charcoal and recrystallized from water, it forms white shining crystals softening at 136° and melting at 142°. The result of the elementary analysis of it is as follows:

Substance,	0.1073 gr.	$CO_2 = 0.2698 \text{ gr.}$	H ₂ C	= 0.0566 gr.
		C = 68.58%	Η	=5.90%
Substance,	0.1111 gr.	$CO_2 = 0.2777 \text{ gr.}$	H_2C)=0.0610 gr.
		C =68.17%	Η	=6.14%
Calculated :	for oxyhydrob	enzoin, C=68.28%	Η	=5.73%

It is, therefore, oxyhydrobenzoin. The present yield was about 1.5 gr. and the total yield 70-80 per cent.

II. Experiments with a sodium bicarbonate solution.

Cathode :	Mercury,	, 50	SQ	. cm.			
Catholyte :	100 CC,	\mathbf{of}	а	saturated	sodium	bicarbonate	solution
	containin	g 5	gr	of salicy	laldehyde	.	

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Anode :	Lead,
Anolyte :	5 % solution of sodium hydroxide.
Current density :	4 amperes/100 sq. cm.
Current :	4 ampere-hours.
Temperatures :	16° – 18°

As salicylaldehyde is insoluble in a sodium bicarbonate solution, it was suspended in the solution and electrolyzed under strong agitation. Moreover, throughout the electrolysis, a constant stream of carbon dioxide was passed through the catholyte to neutralize the free alkali and to keep the solution always weakly alkaline.

The electrolytic solution which was yellow at first gradually got decolorized and was perfectly colorless at the completion of reduction. It was treated in the same manner as before. When, however, it was neutralized with acetic acid to the degree of acidity of carbonic acid, there was no precipitation of hydrobenzoin and the solution remained clear. It was now repeatedly extracted with ether, and the extract dehydrated with anhydrous sodium sulphate and, after dispelling the ether, subjected to steam distillation for the purpose of removing any volatile substance such as aldehydes. The residue in the flask was cooled, filtered from the insoluble substance, and extracted with ether. The ether extract was dehydrated with anhydrous sodium sulphate. When the ether was evaporated off, the substance in the residue crystallized out immediately in a colorless rhombic plate soluble in alcohol, ether, warm benzene, and water. After recrystallizing from a large quantity of ligroin the substance melted at 82° and weighed 4.2 gr., corresponding to 85 per cent of the theoretical yield. The result of the elementary analysis is as follows:

Substance,	0.1429 gr.	CO	$g_2 = 0.3524 \text{ gr.}$	H_2)=0.0848 gr.
		С	=67.25%	Η	=6.64%
Substance,	0.1009 gr.	CO	$b_2 = 0.2511$ gr.	H_2)=0.0621 gr.
		С	=67.90%	Η	=6.89%
Calculated	for oxybenzyl	alc	whol $(C_7H_8O_2)$:		
		С	=67.70%	Η	=6.50%

Saligenin, first obtained by Piria¹ by the decomposition of salicin, was reported as melting at 86° , but according to later literture its true melting-point is 82° , with which my result agrees well.

I Ann. 56, 37 (1845).

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Influence of Temperalure.

All the conditions of electrolysis were kept the same as in the previous experiment, except that the weight of the salicylaldehyde taken was $_2$ gr., and the quantity of the current somewhat less than that necessary for the electrolysis in question : viz. it was only 0.7 ampere-hour. The influence of temperature upon the current efficiency was thus examined.

Temperature °C	Current Efficiency for Saligenin (%)
5°-10°	69
16°-18°	85
22°-26°	82

Table II.

In the neighborhood of 16° the current efficiency is highest, reaching to 87 per cent of the material yield. At lower temperatures the current yield is low, although there is no change in the material yield, which reaches to more than 85 per cent. A small rise of temperature shows no considerable influence, while too high a temperature causes the formation of condensation products, and a diminution both of current and of material yields.

III. Experiments with acetic acid - sodium acetate solution,

All the conditions of electrolysis were the same as in the preceding experiments, except that the catholyte consisted of 5 cc. of glacial acetic acid, 10 gr. of sodium acetate, 100 cc. of water, and 2 gr. of salicylaldehyde. Again in this case, as the aldehyde was insoluble in the solution mixture, it was electrolyzed in a state of suspension with vigorous stirring of the solution. After completion of the electrolysis, the solution was neutralized with sodium bicarbonate to the acidity of carbonic acid and then subjected to the same treatment as before.

A. Influence of Cathodc.

Temperature : $16^{\circ} - 18^{\circ}$ Current density : 4 amperes/100 sq. cm. Current quantity : 0.7 ampere-hour.

Cathode	Current efficiency for Saligenin (%)
Mercury	90
Zinc	65
Lead	61

Table III.

Besides mercury, zinc, and lead, copper and nickel also give the alcohol as the principal product; and the current efficiency is highest with mercury which is highest in over-voltage, giving a material yield of 93 per cent under this condition. Although the current efficiency decreases step by step from mercury to zinc and lead, there is found no great change in the material yield.

B. Influence of Current Density.

All the experimental conditions were the same as before except that mercury was used as cathode.

Current density ampere/100 sq. cm.	Temperature °C	Current quantity ampere-hour	Current yield %
2	12° - 13°	0.75	57
4	16°-18°	0.70	90
6	18°-23°	0.70	76
8	18° 3 0°	0.73	70

Table IV.

For the formation of saligenin, the best result is obtained by the use of 4 amperes/100 sq. cm, of current density. The lower yield at the higher current densities is, however, presumed to be due to the rise of the temperature.

C. Influence of Temperature.

All the experimental conditions were the same as before except that the current density was maintained at 4 amperes/100 sq. cm.

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Table V.				
Temperature °C	Current efficiency in saligenin (%)			
5°~ 8°	54			
16°—18°	90			
28°-35°	51			

The influence of the temperature is, in this case, much greater than when sodium bicarbonate solution is used. The rise of temperature leads to the easy formation of condensation products such as oxyhydrobenzoin and resins, resulting in a great diminution of current and of material efficiency for salicyl alcohol.

D. Influence of the Anode Solution.

All the experimental conditions were the same as before except that the temperature was maintained at from 16° to 18° .

Anode solution (5%)	Current efficiency for saligenin (%)
Sulphuric acid	69
Sodium hydroxide	90

Table VI.

When a strong acid such as sulphuric acid is used in the anode solution, its diffusion into the cathode chamber increases, with the progress of the electrolysis, the hydrogen ion concentration in it, and accelerates the formation of the condensation products, diminishing at the same time the yield of saligenin. When a saturated solution of sodium carbonate was used as anode solution, the material yield was raised to 94 per cent although the current efficiency remained the same as when caustic alkali was used.

Summarising the results described above, the optimum conditions for the production of saligenin by the electrolytic reduction of salicylaldehyde can be formulated as follows: Cathode :Mercury.Catholyte :Although a neutral solution is the ideal, it is impossible to get such a solution, and it is advisable to use as nearly
neutral a solution as possible, such as either a weakly acid solution
like acetic acid - sodium acetate solution, or the saturated sodium bicar-
bonate solution, which is kept weakly alkaline by constantly passing
carbon dioxide throughout the electrolysis.Anolyte :Saturated solution of sodium carbonate.Temperature : $16^{\circ} - 18^{\circ}$.

Current density: 4 amp./100 sq. cm.

As salicylaldehyde is not soluble in such a catholyte and has to be electrolyzed with constant agitation, if a great quantity is used at one time there is danger not only of incurring loss by spattering or volatilizing, but also of easily producing resins under the electric strain, and it is advisable to add small quantities of it in separate portions.

Para-oxybenzaldehyde.

As I obtained by electrolysis of salicylaldehyde, so excellent an amount of saligenin as 94 per cent of material yield, and 90 per cent of current yield, I also tried the electrolytic reduction of p-oxybenzaldehyde under the same conditions and obtained p-oxybenzyl alcohol with the same favourable yield.

P-oxybenzyl alcohol can be obtained by electrolytic reduction of poxybenzoic acid¹, by a purely chemical reduction of p-aldehyde with sodium amalgam in a dilute alcoholic sulphuric acid solution², or by reduction of p-oxybenzamide with sodium amalgam in an alcoholic sulphuric acid solution³, I have, however, succeeded under a simple handling of the electrolytic method, in attaining the favourable result of more than go per cent of current and material yield, without the formation of various by-products.

The best electrolytic conditions given above were adopted and the catholyte consisted of 10 cc. of glacial acetic acid, 10 gr. of sodium acetate, 100 cc. of water and 5 gr. of p-oxybenzaldehyde, which was added in three instalments instead of being added all at once. Acetic

I Mettler, D. R. P. 177490; C. II, 1790 (1906).

² Biedermann, Ber., 19, 2374 (1886).

³ Hutchinson, J. Chem., Soc., 57, 957 (1890); Ber., 24, 175 (1891); Auwer, Daecke, Ber., 32, 3374 (1899).

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acid was added in such a way as just to prevent the anolyte from getting alkaline. When three ampere-hours of current had passed the solution was tested with nitrophenylhydrazine for the aldehyde and it was found to have completely been reduced. The current was then cut off, and the anode solution was neutralized with sodium bicarbonate to the acidity of carbonic acid, repeatedly extracted with ether, and dehydrated with anhydrous sodium sulphate. When the ether was evaporated off there remained white needle crystals. This substance was dissolved in water, filtered The ether extract was from insoluble matter, and extracted with ether. dehydrated and evaporated when nearly pure p-oxybenzyl alcohol separated out to a yield of 4.6 gr., corresponding to 92 per cent of the theoretical. It is almost insoluble in chloroform, benzene, and ligroin, and soluble in When it is heated to about 100° it changes water, alcohol, and ether. to a transparent vitrious mass insoluble in water.

P-oxybenzyl alcohol obtained by Auwer and Daecke melted at 124.5° -125.5° . The substance obtained as above described, when once recrystallized from water, and dissolved in warm chloroform, and precipitated with ligroin, melted at 110° and agreed with the substance obtained by Biedermann, Hutchinson, and Mettler.

The result of an elementary analysis was as follows:

Substance,	0.1278 gr.	$CO_2 = 0.3169 \text{ gr.}$	H_2)=0.0743 gr.
		C = 67.65%	\mathbf{H}	=6.51%
Substance,	0.0898 gr.	$CO_2 = 0.2214$ gr.	H_2C)=0.0545 gr.
		C = 67.23%	Н	=6.79%
Calculated	for p-oxybenz	syl alcohol $(C_6H_8O_2)$:		
		C = 67.70%	Н	=6.50%

With the expectation that, besides the oxyaldehydes, substances that are easily changeable to resins such as vanillin, heliotropin, the halogenaldehydes and cinnamic aldehyde and some other unsaturated aldehydes can be smoothly reduced by the above described reduction method, I am continuing this investigation further.

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