The Electrolytic Oxidation of Alcohols, III.
Electrolytic Oxidation of Benzylalcohol.

By

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Among investigations into electrolytic oxidation reactions of the hydrocarbon sidechains attached to the benzene ring, that on toluene has been already attempted by H. D. Law and F. M. Perkin[1], Merzbacher and Smith[2], and Renard[3], etc. The oxidation products which varied according to the conditions of electrolysis consisted chiefly of benzaldehyde, and the formation of benzoic acid was scarcely to be noticed while the maximum current yield was reported to be 14 percent, and the yield in material 15 percent for benzaldehyde. Later on, Fichter and Stocker[4] have pointed out that by the electrolytic oxidation of toluene, hydroquinone and toluhydroquinone are formed side by side with benzaldehyde, thus showing a difference in progress of reaction of the electrolytic oxidation from that of the purely chemical oxidation of benzene derivatives. In 1920 Fichter[5] investigated the electrolytic oxidation of benzaldehyde and benzoic acid, and attempted an elucidation of the mechanism of reaction in the electrolytic oxidation of toluene.

Notwithstanding this, there is not yet any record found of any experimental study of the electrolytic oxidation of benzylalcohol which is considered to be the first oxidation stage in the progress of the electro-

1 Chem. News, **91** (1904), 54 · Ibid., **92** (1905), 69 ; Trans. Farad. Soc., **1** (1905), 31.
2 J. Am. Chem. Soc., **22** (1900), 723.
3 Compt. rend., **91** (1880), 175.
4 Ber., **47** (1914), 2003.
5 Helv , Vol. III (1920), 22.

lytic oxidation of toluene. If in electrolytic oxidation toluene changes to benzaldehyde through the stage of benzylalcohol thus :

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2OH \rightarrow C_6H_5CHO$$

then the electrolytic oxidation of benzylalcohol may also be expected chiefly to stop at the stage of benzaldehyde without so far proceeding as to give benzoic acid. To see if such really be the case the present investigation was undertaken.

Material used : Benzylalcohol B. P. $204° - 206°$ C., Sp. Gr. $1.0445 \dfrac{25°}{25°}$

I. Reaction in an Acid Electrolytic Solution

Since it was found by a preliminary experiment, that the oxidation efficiency was increased by stirring the electrolytic solution while the decomposition was accelarated by the rise of temperature, the solution was always stirred and the temperature kept at or below the room temperature.

As to the stirring device, a porous cylinder containing the cathode solution was immersed into the anode solution and made to rotate, and it was found to work very effectively. As is shown in the illustration, the porous cylinder was tightly stoppered with a rubber stopper through which a stout glass tube carrying a wire connected with a cathode passes, and this glass tube served as a rotating shaft. A little mercury was poured into this rotating shaft and a conducting wire from a cathode terminal was dipped into it. Two slender glass rods were attached to the wall of the cylinder to make the stirring effective.

Treatment after Electrolysis :

The brown-colored electrolyzed solution, acid with sulphuric acid, was saturated with sodium sulphate and repeatedly extracted with ether. To the ether extract a conc. solution of sodium sulphite (prepared by dissolving 20 gr. in 60 cc. of water) was added and the mixture set aside for 24 hours with occasional shaking. The addition product of benzaldehyde and acid sodium sulphite $C_6H_5CH(OH)SO_3Na$ which separated out was then filtered and the acid sodium sulphite solution remaining below the
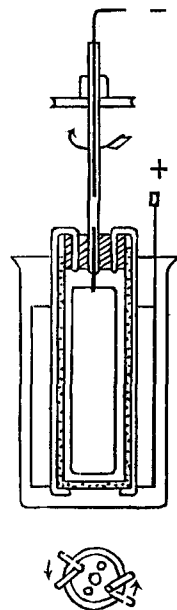
ether solution was separated, and, after neutralization with sodium carbonate, was subjected to steam distillation. If the aldehyde appeared in the distillate in an oily form, it was dissolved by addition of a small volume of alcohol and made up to 1 litre. Out of the total volume of 1 litre, 100 cc. were taken out for precipitating the aldehyde with phenylhydrazine. From the weight of the benzylidenephenyl-hydrazine (m. p. 153°) thus obtained, the total weight of the aldehyde in the whole distillate was calculated. To this amount of the aldehyde the amount calculated from the addition product of acid sodium sulphite was added and the grand total was taken as the final yield of the benzaldehyde.

The ether extract from which the benzaldehyde was separated was now shaken with a sodium carbonate solution in order to isolate the acidic products in it. When the sodium carbonate solution was separated and acidified with sulphuric acid, benzoic acid (m. p. 120°) was liberated.

Finally, the residual ether extract was evaporated and a small quantity of a brown liquid was obtained which sometimes contained, beside the original benzylalcohol that escaped the reaction, a small quantity of benzyl-benzoic acid, distilling between 320° and 340°. There was always found a small quantity of a tarry residue after distillation.

(1) Anode: Lead peroxide (12×18.5) 222 sq. cm.
       Anode solution: 300 cc. of 0.5 N–H_2SO_4 to which 20 g. of the sample were added.
       Cathode: Iron plate.
       Cathode solution: 0.5 N–H_2SO_4
       Temperature: $14° \pm 1°$.

Current quantity	Current density amp /sq. cm.	Sample used	Sample recovered	Benzaldehyde		Benzoic acid	
				Current yield	Material yield	Current yield	Material yield
24 amp. hours	0.009	20 g	1.0 g.	4.18 g.		7.50 g.	
				8.79%	22.39%	27.45%	34.94%
do.	0.018	20	1.5	3.62		8.01	
				7.62	19.94	29.30	38.32
do.	0.027	20	2.4	3.66		7.2	
				7.71	21.18	26.34	36.21
18 amp. hours	0.0135	20	2.8	7.32		5.50	
				30.53	43.34	26.83	28.31

From the above results it may be concluded that the variation of current density does not exert any great influence upon the yield of the reaction product, while the variation of current quantity exerts a rather considerable influence upon it. Thus while the yield of the aldehyde decreases with the increase of current quantity, the yield of the acid does not show any corresponding increase, showing that, above a certain limit of current quantity, the current is expended not simply for the oxidation of the aldehyde into acid but for the oxidation of the benzene nucleus, or some destructived oxidation, thus resulting in the decrease of its oxidation efficiency. When, for 20 g. of the material, a far greater quantity of current was used than the amount calculated as necessary, the yield of benzoic acid was about 8 g. With a still greater excess of current, there was found, besides the nuclear and destructive oxidation, the formation of a phenol derivative which gave a purple color reaction with ferric chloride.

(2) The Influence of the Electrodes.

Anode solution : 300 cc. of $1 N - H_2SO_4$ with 20 g. of the material added.

Cathode : Lead.

Cathode solution : Similar to the anode solution.

Temperature : $15° \pm 1°$.

Anode	Current	Sample used	Sample recovered	Benzaldehyde		Tarry residue	Fraction 210°—260°
				Current yield	Material yield		
Platinum foil 7.1 × 5.1 = 36.21 sq. cm.	0.0829 amp./sq. cm. 24 amp. hours	20 g.	14.2 g.	3.924 g.		about 1 g.	about 0.5 g.
				8.26%	68.93%		
Platinum gauge 5.0 × 11.0 = 55 sq. cm.	0.0545 amp./sq. cm. 9 amp. hours	20	13.1	4.276		,, 1	,, 1
				24.01	63.14		
Platinum gauge 5.0 × 11.0 = 55 sq. cm.	0.0545 amp./sq. cm. 24 amp. hours	20	12.9	4.121		,, 1.5	,, 0.5
				10.92	59.13		
Gold foil 8 × 7.5 = 60 sq. cm.	0.0667 amp./sq. cm. 24 amp. hours	20	13.3	3.309		,, 1	,, 0.7
				6.97	50.31		

As may be seen from the above table, when platinum and gold electrodes are used, the oxidation efficiency of the current is far lower than when the lead peroxide electrode is used. Moreover, in the former cases, there is hardly any formation of benzoic acid noticeable even with the

expenditure of 24 ampere-hours of the current. The fractions boiling at $210° - 260°$ being very small in amount were gathered and subjected to repeated fractionation, but no substance giving a constant boiling-point was separated except that a little more benzylalcohol was recovered. The tarry residue, though small in amount, was always found even when the fractionation was carried on under diminished pressure or in a current of carbon dioxide gas.

(3) The Influence of the Concentration of Sulphuric Acid.

Anode : Lead peroxide, 222 sq. cm.

Cathode : Iron plate.

Cathode Solution : The same as the anode solution.

Temperature : $15° \pm 2°$

Current density : 0.01802 amp./sq. cm.

Current quantity ; 24 amp. — hours.

Anode Solution 300 cc. H_2SO_4	Current quantity amp.-hours.	Material used	Material recovered	Benzaldehyde		Benzoic acid		Tarry resid.
				Current yield	Material yield	Current yield	Material yield	
0.5 N	24	20 g.	1.5 g.	3.62 g.		8.01 g.		
				7.62%	19.94%	29.30%	38.32%	
1 — N	24	20	0.8	3.58		8.21		less than 1 g.
				7.53	19.00	30.03	37.85	
2 — N	24	20	—	5.661		8.15		
				11.92	28.84	29.82	36.08	
2 — N	18	20	2.0	5.633		7.20		
				15.81	31.88	35.12	35.41	

In the neighborhood of the sulphuric acid concentration of $2 - N$, the total oxidation efficiency is greatest, while the decomposition is correspondingly great and the electrolytic solution is colored a deep brown. In the electrolysis of sulphuric acid solutions phenol derivatives are found only when a great excess of current is passed, and as is shown by the instances given above, the passage of a current of 24 amperehours against the calculated quantity of 19.84 am.-hours does not induce the formation of any phenol derivatives detectable by the ferric chloride reaction. Yet even in these cases, it sometimes happens that a minute quantity of a coloring matter giving a distinct purple colour by an alkali is contained in the tarry matter produced to a more or less extent. It

may be conjectured that the coloring matter[1] here mentioned is formed by the condensation of the phenol produced in minute quantity in the electrolytic solution with benzaldehyde by the action of the accumulated sulphate ions on the anode surface.

II. Reactions in an Alkaline Electrolytic Solution.

Treatment after electrolysis.

The alkaline solution after electrolysis was repeatedly extracted with ether.   The ether extract was completely dehydrated by means of anhydrous sodium sulphate and then the ether distilled off.   The remaining liquid was subjected to fractional distillation in a carbon dioxide atmosphere to prevent the oxidation of benzaldehyde.

The electrolyzed alkaline solution, thus deprived of benzaldehyde and benzylalcohol by ether extraction, was now completely neutralized with sulphuric acid and concentrated by the low temperature distillation under diminished pressure.   From the resulting liquid benzoic acid was liberated by acidification.

(1)   Anode :   Platinum gauge, 55 sq. cm.
   Anode solution :   To 300 cc. of $2N-NaOH$ solution were added
                      20g. of benzylalcohol.   The mixture was well
                      stirred in a closed anode chamber.
   Cathode :   Nickel gauge.
   Cathode solution :   The same as the anode solution.
   Current density :   0.07273 amp./sq. cm.
   Temperature : $25° \pm 2°$.

Current	Material		Benzaldehyde		Benzoic acid	
	taken	recovered	Current yield	Material yield	Current yield	Material yield
24 amp.-hours	20. g.	0.8 g.	12.5 g.		2.85 g.	
			26.31%	66.33%	10.42%	13.14%
28.8 amp.-hours	20	—	9.8		2.9	
			17.19	49.93	8.84	12.83

In this case as in the case of electrolysis in an acid solution, the increase of current quantity does not practically accompany the increase of the yield of the acid while that of the aldehyde actually decreases.

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1   Melzer, Zeit. f. anal. Chem., **37** (1898), 345.

Thus the current efficiency in oxidizing the aldehyde into benzoic acid is very slight, and not only does it decrease beyond a certain quantity of current, but it even induces a decomposition reaction at the same time. If the volume of the gas evolved in the tightly sealed anode chamber is examined the evolution of oxygen is found to increase in proportion to the duration of the electrolysis. The carbonic acid formed by the decomposition reaction is completely absorbed by the alkaline electrolytic solution. In 500 cc. of the anode gas collected under the above-mentioned condition, the presence of hydrogen could not be detected.

(2) All the conditions were made the same as the above, except that the temperature was kept at $0°$.

Current	Material		Benzaldehyde		Benzoic acid	
	taken	recovered	Current yield	Material yield	Current yield	Material yield
24 amp.-hours	20 g.	1 g.	10.8 g.		2.7 g.	
			22.74%	57.90%	9.88%	12.58%

As may be seen from the results, even when the solution is cooled down to $0°$ during the electrolysis, it gradually assumes a brown colour accompanied by a destructive oxidation and the yield of the products remains unchanged.

(3) The Influence of the Concentration of Alkalis.

i) The temperature was kept at $25° \pm 2°$ and the electrodes, current density, current quantity etc. remained the same as before.

Anode solution	Material		Benzaldehyde		Benzoic acid	
	taken	recovered	Current yield	Material yield	Current yield	Material yield
0.5 N NaOH	20 g.	0.8 g.	9.10 g.		2.9 g.	
			19.15%	48.28%	10.61%	13.38%
1 N NaOH	20	0.5	10.8		2.87	
			20.74	56.43	10.50	13.03
2 N NaOH	20	1.5	11.0		2.85	
			23.16	60.57	10.42	13.63

ii) The anode solution consisted of 300 cc of $2N-Na_2CO_3$ solution mixed with 20 g. of the material. Current quantity and the other con-

ditions all remained the same as before.

2 – N Na₂CO₃	20 g.	2 g.	12.50 g.		Benzoic acid could not be separated.
			26.31 %	70.74 %	

In the electrolysis of alkaline solutions, the yield of benzaldehyde is greatest when a sodium carbonate solution is used as the anode solution and its material yield reaches 70.74% while the formation of benzoic acid is scarcely noticed.

When the electrolyzed solution was completely extracted with ether and the benzoic acid liberated was filtered off, the solution still retained a deep brown colour. Although various organic solvents were tried in order to obtain some further electrolytic products from this coloured solution, their extraction was found to be a difficult matter. However, a mixture of amylalcohol and ether repeatedly shaken with the deep brown solution, extracted almost completely the colouring matter from it. When this alcohol-ether extract was separated and subjected to distillation under a diminished pressure, a black tarry residue weighing about 1 g. was obtained, the nature of which has not yet been made clear.

From the experimental results so far described it may be concluded that the electrolytic oxidation of benzylalcohol generally takes place so as to produce benzoic acid as well as benzaldehyde, and differs from that of toluene which, as was stated before, does not proceed further than the aldehyde formation. In an acid solution when platinum is taken as the anode, and also in a sodium carbonate solution, benzylalcohol is, however, not oxidizable to benzoic acid, benzaldehyde being the final oxidation product.