

On the Electrolytic Reduction of Aldehydes. Part II. Metanitrobenzaldehyde.

By

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ABSTRACT.

Electrolytic reduction of nitrobenzaldehyde in a dilute sulphuric acid solution was minutely studied, lead and copper being used as the cathode, and the influence of current density, temperature, and concentration of sulphuric acid on the reduction were determined. Contrary to the results obtained by many authors, it was found that by use of a lead cathode and a dilute sulphuric acid solution, a nearly quantitative yield of m-amidobenzyl alcohol could be obtained, while a copper cathode gave rise to the intermediate condensation product. The reason for the different results brought about in the writer's experiments and those of other authors, and also the conditions necessary for procuring the best yield of the amidobenzyl alcohol were sought.

Electrolytic reduction of m-nitrobenzaldehyde, hitherto investigated by several authors, is reported to have resulted in the production of complex substances which are formed by condensation of partially reduced products. By electrolysing a concentrated sulphuric acid solution Gattermann¹ and Always² obtained nitrobenzylidene metaaldehyde phenylhydroxylamine. In their experiments, therefore, only a partial reduction of the nitro group to the hydroxylamine stage took place, leaving the whole aldehyde group and a part of the nitro group unchanged. According to the latter author the condensation product above described undergoes further reduction and produces the corresponding azoxy compound, but in no case could reduction of the aldehyde group be attained. Kaufmann

¹ Ber., **29**, 3039 (1896).

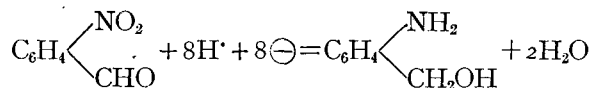
² Ibid., **36**, 23 (1903); Zeit. Electrochem., **3**, 373 (1897).

and Hof¹ and also Lob² investigated the reduction in an alcoholic alkaline solution and obtained azoxybenzoic acid and azoxybenzyl alcohol. But the production of benzoic acid and benzyl alcohol in this case is a purely chemical process and the part played by the electrolytic reduction was to change the nitro group into the hydroxylamine group.

As it is rather inconceivable that presence of a nitro group so much influences an aldehyde group as to make its reduction impossible or at least very difficult a through investigation into the electrolytic reduction was deemed very interesting.

As the cathode, lead and copper were chosen, the former as the electrode of high over-voltage, and the latter as that of moderate over-voltage, having at the same time a special catalytic action on reduction of the nitro group.

From the result of previous experiments performed by Gattermann and others it is clearly seen that in a concentrated sulphuric acid solution electrolytic reduction chiefly takes place in the nitro group and leaves the aldehyde group unacted on, and this may be conceived as the precise reason why amidobenzyl alcohol was not formed only the intermediate condensation product having been formed. In order to ensure the production of amidobenzyl alcohol both the nitro and the aldehyde group must be reduced equally and quickly, so that no room is left for the intermediate product to enter into secondary reactions. For this reason an alcoholic solution containing dilute sulphuric acid (about 10%) was taken as the catholyte and electrolysed with a carefully prepared lead cathode maintaining current density at about 5 amp/100 sq. cm. As was expected, the result was quite satisfactory, *m*-amidobenzyl alcohol being produced with a yield of more than 90%. The reduction progressed very smoothly according to the following equation:



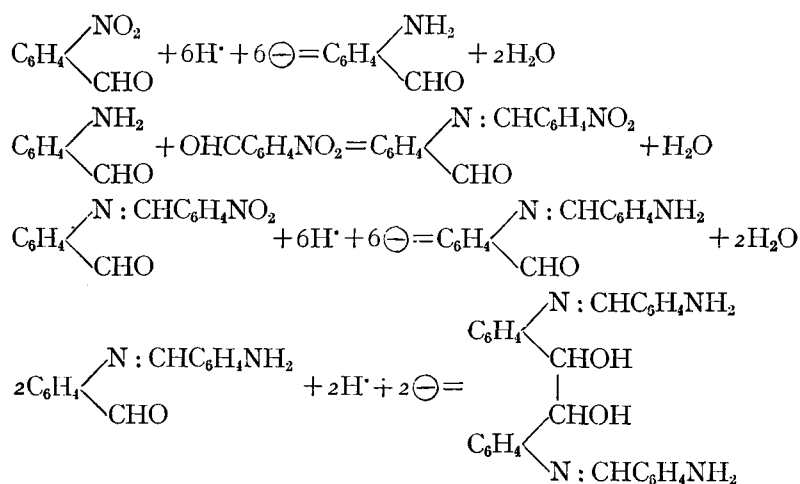
The results of many experiments showing the influence of current density, temperature, and concentration of sulphuric acid on the reduction will be seen in the annexed tables and figures given in the experimental part.

When copper was used as cathode not only was the current efficiency far lower, but the reduction came quickly to a standstill, and

¹ Chem. Zeit., **20**, 242 (1896).

² Zeit. Electrochem., **5**, 456 (1899); Ber., **31**, 2201 (1898).

m,m-diamidobenzalamido-hydrobenzoin was produced as a main product together with small quantities of azoxybenzaldehyde and amidobenzyl alcohol. From this result it is seen that the nitro group is reduced to the amido group almost completely with copper which acts on it as a specially effective cathode, and that as long as the nitro group still remains there; reduction is solely concentrated upon it and does not affect the aldehyde group whose reduction commences only at the moment when that of the nitro group has completed. This also accounts for the condensation product obtained by the writer being different from those obtained by other authors. The reaction may be formulated as follows :



Experimental Part.

Metanitrobenzaldehyde used in the experiment was prepared from benzaldehyde by nitration and purified by repeatedly crystallizing from 50% acetic acid. It melted at 58°.

I. Copper cathode.

The apparatus was so constructed that the cell serving as the anode compartment acted as an agitator of the cathode solution. For this purpose wire connecting the anode was fused to a glass tube which was tightly attached to the cell by means of a rubber stopper, and the glass tube was made to rotate together with the cell, as is seen in figure 1.

Catholyte: H₂SO₄ (1.2) 100 ccm + alcohol 160 ccm.

nitrobenzaldehyde 10 gr.

Anolyte: H_2SO_4 (1.1).

Cathode: Copper plate 150 sq. cm.

Anode: Platinum wire.

Current density: 6 amp./100 sq. cm.

The electrolysis was commenced at the room temperature. The temperature of the bath, however, gradually became higher and at last began to boil, and at the same time its colour changed from yellow to deep red. After the electrolysis was over the catholyte was poured into ice and left to stand for a night. A resinous mass of deep red colour separated out. This was treated with benzene, and to the benzene solution ligroin was added, when a yellowish substance crystallized out. The needle crystals after having been purified with charcoal and recrystallized from alcohol melted at 129° . Their alcoholic solution was easily seen to react with phenylhydrazine and produce an orange yellow coloured hydrazone melting at 192° - 193° .

0.1079 gr substance gave 0.2625 gr CO_2 and 0.0400 gr H_2O ; $\text{C}=66.33\%$, $\text{H}=4.15\%$ (Calc. for $\text{C}_{14}\text{H}_{10}\text{O}_3\text{N}_2$, $\text{C}=66.15$, $\text{H}=3.97$). The substance was thus proved to be azoxybenzaldehyde.

The acid solution filtered from the resinous substance was distilled under reduced pressure to remove alcohol and then neutralized with sodium carbonate, whereupon a large quantity of a yellow amorphous solid was precipitated.

As it was insoluble in all other solvents, it was dissolved in hydrochloric acid and again precipitated with sodium carbonate. It formed a platinum double salt and picrate.

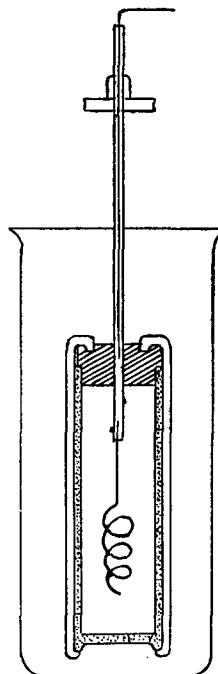
0.1341 gr platinum double salt gave 0.0305 gr Pt on ignition; $\text{Pt}=22.74\%$ (Calc. for $\text{C}_{23}\text{H}_{26}\text{O}_2\text{N}_2\text{H}_2\text{PtCl}_6$, $\text{Pt}=22.70$).

0.1540 gr substance gave 0.4203 gr CO_2 and 0.0730 gr H_2O ; $\text{C}=74.25\%$, $\text{H}=5.30\%$ (Calc. for $\text{C}_{23}\text{H}_{26}\text{O}_2\text{N}_2$, $\text{C}=74.64$, $\text{H}=5.02$)

0.1333 gr picrate gave 0.2604 gr CO_2 and 0.0466 gr H_2O ; $\text{C}=53.27\%$, $\text{H}=3.91\%$ (Calc. for $\text{C}_{40}\text{H}_{32}\text{O}_{16}\text{N}_{10}$, $\text{C}=52.84$, $\text{H}=3.55$). From these results the substance was decided to be m,m-diamidobenzalamido-hydrobenzoin.

The solution from which above hydrobenzoin was filtered off was

Fig. 1.



repeatedly extracted with chloroform, and after having been well dried with anhydrous sodium carbonate the chloroform solution was evaporated to drive off the chloroform. When a brown residue thus isolated was recrystallized from benzene-ligroin and decolourized with charcoal, a substance crystallizing in needles and melting at 92° was obtained. It gradually changed its colour to brown in air.

0.1334 gr substance gave 0.3328 gr CO_2 and 0.0889 gr H_2O ; C=68.01%, H=7.45% (Calc. for $\text{C}_7\text{H}_9\text{ON}$, C=68.29, H=7.31) The substance was thus confirmed to be m-amidobenzyl alcohol.

II. Lead cathode.

In this case a cell was used as the cathode compartment and hydrogen gas there evolved was measured in order to learn the reduction efficiency, which was calculated as a percentage volume of hydrogen consumed in every one minute. A detonating gas coulometer was inserted in the circuit for comparison.

1. Influence of current density.

Catholyte: H_2SO_4 (1.2) 40 ccm + alcohol 100 ccm + nitrobenzaldehyde 5 gr. Temp.: 25° - 26°

Anolyte: H_2SO_4 (1.1); Anode: PbO_2

Table I.

Current density (amp/100sq. cm.)	Quantity of Electricity (amp. hour)	Yield of Amidobenzylalcohol (%)
6	16	83.5
5	15	93.4
4	14	92.1
3	11	89.1
2	12	87.2

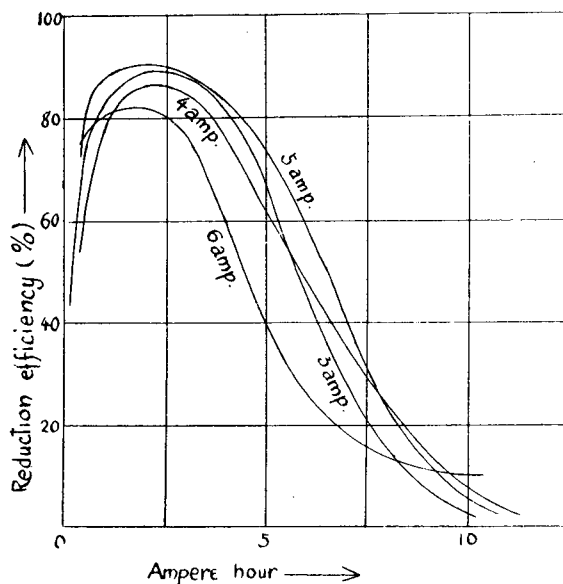
From this table it appears that current density has no great influence on the yield of the amido-alcohol.

The relation between current density and reduction efficiency is shown in the following table and figure.

Table II.

Current Density							
3 amp/100 sq. cm.		4 amp/100 sq. cm.		5 amp/100 sq. cm.		6 amp/100 sp. cm.	
Elec. Quantity (amp. hour)	Reduc. Efficiency (%)	Elec. Quantity (amp. hour)	Reduc. Efficiency (%)	Elec. Quantity (amp. hour)	Reduc. Efficiency (%)	Elec. Quantity (amp. hour)	Reduc. Efficiency (%)
0.25	46.84	0.40	54.04	0.58	72.49	0.50	76.03
0.60	72.64	1.00	77.47	1.17	89.60	2.50	82.28
1.00	82.29	2.30	86.86	3.75	85.07	3.50	70.78
2.50	88.98	4.00	75.56	5.00	74.57	4.50	49.61
4.25	80.37	5.30	58.92	6.25	54.01	5.50	31.69
5.00	64.83	6.60	41.24	7.08	40.94	7.50	15.79
6.00	44.83	8.00	23.29	8.00	21.53	8.50	12.41
7.50	20.25	9.70	8.50	9.20	9.82	9.50	11.40
9.25	5.60	10.60	4.17	10.40	3.22	10.50	10.38
10.25	1.63	12.50	0.51	11.70	1.29		

Fig. 2.



2. Influence of temperature.

Current density : 3 amp/100 sq. cm. The other condition were the same as in (1).

Table. III.

Temp.	Quantity of Electricity (amp. hour)	Yield (%)
5°-6°	12.5	79.8
22°-25°	11.0	89.1
35°-36°	9.0	89.7

Both the yield and reduction efficiency were seen to be best at 25°-35°.

Table IV.

Temperature					
5°-6°		22°-25°		35°-36°	
Time (mine)	Efficiency (%)	Time (min)	Efficiency (%)	Time (min)	Efficiency (%)
5	39.41	5	46.84	5	81.79
10	50.16	12	72.61	10	92.81
40	61.46	20	82.29	20	95.98
80	60.33	50	88.98	80	85.88
95	54.16	85	80.37	93	76.30
115	46.26	100	64.83	120	37.30
185	22.74	150	20.25	130	23.64
220	16.50	185	5.60	145	10.00
250	11.40	205	1.63	165	2.27

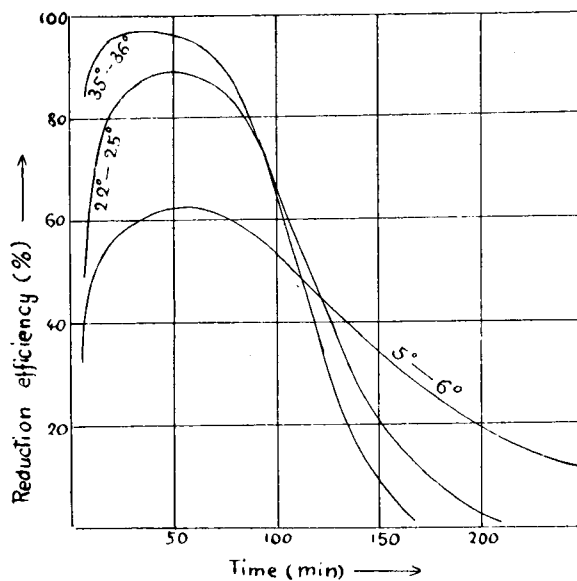
3. Influence of concentration of H₂SO₄.

In all cases 40 c.c of sulphuric acid of different density were added to 100 c.c of alcohol, all other conditions being the same as in (2).

Table. V.

Density of H ₂ SO ₄	Amp. Hour	Yield (%)
1.15	12.0	82.3
1.18	11.5	89.1
1.20	11.0	89.1

Fig. 3.

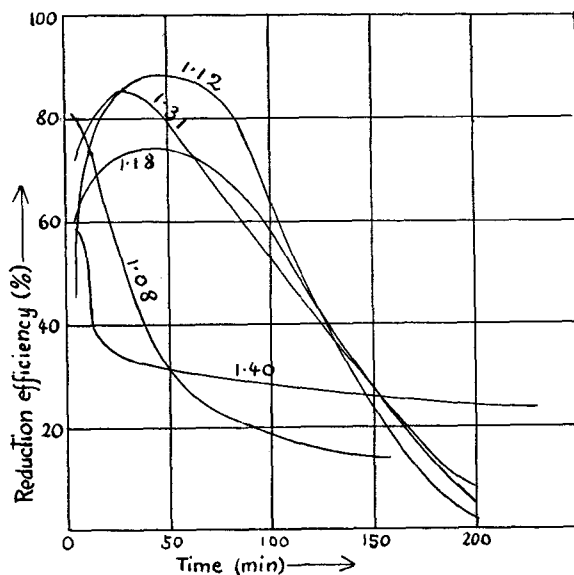


From the above results it is concluded that the best yield and reduction efficiency were procurable when the cathode solution contained about 10% of sulphuric acid. The relation will be clearly seen in the following table and figure.

Table VI.

Specific Gravity									
1.08		1.18		1.20		1.31		1.40	
Time (min)	Efficiency (%)	Time (min)	Efficiency (%)	Time (min)	Efficiency (%)	Time (min)	Efficiency (%)	Time (min)	Efficiency (%)
5	81.47	5	60.99	5	46.84	5	71.94	6	58.16
18	65.58	20	71.27	12	72.61	22	84.84	10	54.00
40	38.17	55	72.98	20	82.92	65	71.47	30	31.62
50	30.94	90	66.15	50	88.98	110	47.11	120	29.73
60	26.65	110	53.84	85	80.37	135	35.35	135	27.05
85	22.76	135	36.20	100	64.83	160	21.56	150	25.23
100	21.31	165	17.72	150	20.25	185	10.44	175	24.31
130	14.78	200	4.37	205	1.63	198	6.97	230	24.07

Fig. 4.



4. Comparison of lead and copper cathodes.

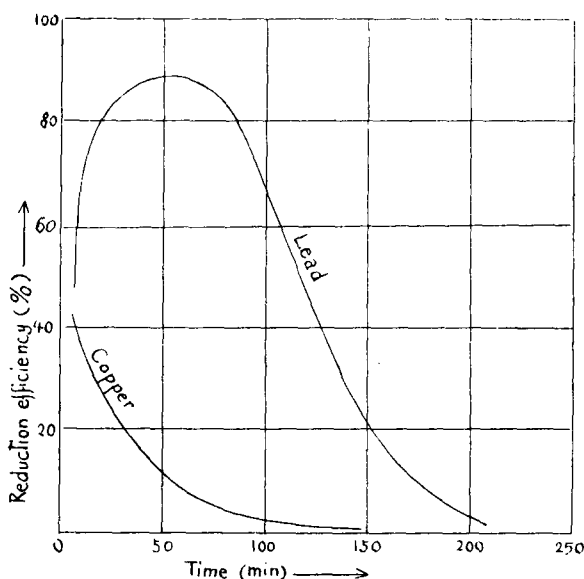
All the conditions used in the experiment were the same as in (2), and the progress of reduction with a lead cathode was traced and compared with that with a copper cathode. As was stated before, the difference between lead and copper as the cathode in the reduction of

Table VII.

Cathode			
Lead		Copper	
Time (min)	Efficiency (%)	Time (min)	Efficiency (%)
5	46.84	2	45.48
12	72.61	5	39.28
50	88.98	20	25.97
85	80.37	40	15.63
100	64.83	55	8.53
150	20.25	85	3.32
205	1.63	105	2.60

m-nitrobenzaldehyde may well be explained by the fact, that while lead acts as a powerful reducing cathode for both the aldehyde and the nitro group, copper reduces the latter group selectively, having less reducing action on the former group. This difference will be seen in the table VII and figure 5 which clearly show that the reduction with a copper electrode, though not much different from that with a lead electrode at the outset of electrolysis, comes to a stand-still nearly at half time.

Fig. 5.



In conclusion, the best conditions for reduction of *m*-nitrobenzaldehyde to the corresponding amido-alcohol may be given thus:

Cathode and anode: Lead; Temp.: 25°-35°

Cathode solution: Alcoholic solution containing
10% of H₂SO₄.

Current density: 5 amp/100 sq. cm.

The author wishes to express his sincere thanks to Professor M. Matsui at whose suggestion the work was carried out.