On the Electrolytic Reduction of Aldehydes, Part VI. Complete Reduction of the Carbonyl Group

By

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Though an aldehyde is reducible electrolytically to the corresponding alcohol and pinacone with ease, its complete reduction to hydrocarbon can only be brought about under some specific conditions.   Tafel and Schepss[1] found that both aldehyde and ketone are best reduced to hydrocarbon when cadmium is used as the cathode.   Since that time cadmium has been regarded as the only cathode which can be used for complete reduction of the carbonyl group. Inferring from the close analogy existing between cadmium and zinc, and from the fact that zinc acts chemically as such an effective reducing agent that it is practically employed universally in many chemical reductions, and that its over-voltage for evolving hydrogen is notably higher than that of cadmium, it is conceivable that a zinc cathode will give rise to the formation of hydrocarbon with an efficiency perhaps surpassing that of cadmium or at least similar to it.

To verify this experimentally I undertook the electrolytic reduction of anisaldehyde, salicylaldehyde, paraoxybenzaldehyde, vanillin and piperonal, and observed that the formation of hydrocarbons was always greater at the zinc cathode than at the cadmium. Especially salicylaldehyde which does not change to the corresponding cresol when reduced with the latter elect-

1   Ber., **44**, 2148 (1911); Schepss, Ber., **46**, 2566 (1913), Tafel, Ber., **42**, 3146 (1909).

rode could at the former electrode be transformed into it with 65% yield.

As I have frequently observed, the presence of alcohol in a large quantity effects the electrolytic reduction of aldehyde in such a way as to lead to the formation of condensation-products such as pinacone or still more complicated resinous matter, thus preventing the formation of simple reduction-products like alcohol and hydrocarbon. As a most typical example of this the reduction of vanillin may be mentioned here. While vanillin is reduced in a sulphuric acid solution to o-creosol with 75 % yield, the same reduction can scarcely be observed when the cathode solution containing much alcohol is electrolysed. The electrolytic reduction of aldehyde and ketone in acid sodium sulphite solutions[1] and also that of aldehyde in caustic soda solutions[2] generally take place in a preicsely similar manner chiefly producing condensation-products. Perhaps these reactions may be regarded as belonging to the same kind of reduction, that is, reduction of the addition-products of aldehyde or ketone such as

$$RCH\left\langle{}^{OH}_{SO_3Na,}\right. \qquad RCH\left\langle{}^{OH}_{ONa,}\right. \qquad RCH\left\langle{}^{OH}_{OC_2H_5,}\right.$$

which naturally differs from that of free aldehyde or ketone.

Erich Müller[3] tried to explain the reduction of aldehyde and ketone, representing its progress in the following scheme :

1   Kauffmann, Z. Elektrochem., **2**, 1265 (1896) ; **4**, 361 (1898).
2   Law, J. Chem. Soc., **89**, 4512 (1906).
3   Z. angew. Chem., **35**, 698 (1922).

Ingenious as it is, Muller's theory seems still insufficient to explain the above-stated difference existing between the electrolytic behaviour of aldehyde and of its addition-products.

Experimental

Into a glass cylinder having a diameter of 6 cm. which was used as the anode chamber, a cell of about 200 cc. capacity (diameter, 4.5 cm.) was placed as the cathode compartment. Zinc amalgam used as the cathode was prepared by electrolysing a concentrated solution of zinc sulphate till mercury taken as the cathode solidified completely. The cathode solution consisted of sulphuric acid of different dilution or of alcoholic sulphuric acid into which 5 grams of aldehyde to be reduced were added little by little on vigorous agitation. A platinum plate was dipped as the anode in 30 % sulphuric acid contained in the cell.

1. Anisaldehyde

By electrolyzing anisaldehyde in 5 % alcoholic sulphuric acid solution with a copper cathode, Law[1] obtained anisic alcohol (70–75%) and p-methyl anisole (5%). Tafel and Schepss[2] used cadmium in place of copper and by this means raised the yield of p-methyl anisole to 37%. Examining the influence of the temperature, current density and concentration of the sulphuric acid in the cathode solution the latter authors determined the best conditions for the production of p-tolyl methyl ether and working under those conditions a 60 % yield was finally procured. The conditions they used were: Anode solution—20 gm. of anisaldehyde + 60 c.c. of water + alcohol to 180 c.c + 15 gm. of conc. sulphuric acid; Temperature —below 25°; Current density—30 amp./100 sq. cm.

I conducted a series of experiments to reduce anisaldehyde to p-tolyl methyl ether using zinc amalgam as the cathode. The cathode solution after electrolysis was diluted with much water and treated with ether in order to extract the substances dissolved in it. To the ether extract, calcium chloride was added to remove alcohol and water from it, and after the ether had been evaporated off, it was distilled under reduced pressure. The portion distilling at 66°–70° at 14 mm. pressure was collected. It boiled at 175° at ordinary pressure. It was analysed with

1 J. Chem. Soc., **91**, 748 (1907).

2 Loc. cit.

the following results :

    0.1416 gm. substance gave 0.4065 g CO_2 and 0.1039 g H_2O,

    C=78.29%,   H=8.20% ;   Calc.   C=78.69%,   H=8.20%

The results of experiments conducted under various conditions are given thus :

Table I

No.	Catholyte			Current density amp./100 sq. cm.	Current quantity amp.-hour	Temperature °C	p-Tolyl methylether %
	Sulphuric acid		Alcohol cc				
	%	cc					
1	30	80	—	36	18	20—25	10
2	50	80	—	48	20	20—25	30
3	60	80	—	30	17	15—25	39
4	60	80	—	36	18	20—25	40
5	60	80	—	36	18	30—35	31
6	60	80	—	48	20	20—25	38
7	60	80	—	60	25	30—35	32
8	70	80	—	30	30	12—16	51
9	70	80	—	36	30	12—20	45
10	70	80	—	48	28	23—28	40
11	70	80	—	48	25	20—25	43
12	80	80	—	30	20	20—25	5
13	40	50	30	30	15	12—16	38
14	60	50	30	30	15	12—16	58
15	60	50	30	48	16	20—25	56
16	60	50	30	60	12	30—35	60
17	60	50	30	18	15	5—8	51
18	70	50	30	30	15	15—18	49
19	70	50	30	18	15	8—18	56
20	60	30	50	30	15	10—15	22
21	60	20	50	30	15	12—15	58
22	60	60	20	30	15	10—15	56
23	60	60	20	42	18	18—21	58
24	60	60	20	72	15	35—40	68
25	60	70	10	30	15	10—15	33

    When the cathode solution contains no alcohol the electrolysis is greatly effected by temperature, the more p-tolyl methyl ether being given the lower the temperature is (No. 1—No. 12). The concentration of the sulphuric acid should be maintained at about 60-70 %, for the more concentrated acid has the effect of resinising the aldehyde. The

greater current density gives the better yield. But when the current density becomes greater it is very difficult to regulate the temperature of the bath, which must always be kept low. In experiment from No. 13 to No. 25 it is seen that the presence of a certain amount of alcohol in the cathode solution favours the formation of p-tolyl methyl ether even at higher temperatures, and in consequence the current density can be made greater to increase the yield of the product. As was stated before, however, an excess of alcohol has quite the contrary effect (No. 20).

2. Salicylaldehyde

In the electrolytic reduction of salicylaldehyde hitherto conducted in an alcoholic sulphuric acid solution[1], neither the corresponding alcohol nor phenol was obtained. I was able, for the first time, to reduce the aldehyde to saligenin at the mercury cathode by using a neutral cathode solution[2]. It was now found that at the zinc amalgam cathode the aldehyde can be reduced to o-cresol in a sulphuric acid solution with about 66% yield. The electrolysis and also the treatment of the cathode solution after electrolysis were conducted in the same way as in the previous experiment, and o-cresol obtained was purified by distilling it under 20 mm.

Table II

No.	Catholyte			Current density amp./100 sq. cm.	Current quantity amp.-hour	Temperature °C	o-Cresol %
	Sulphuric acid		Alcohol cc				
	%	cc					
1	15	80	—	30	15	10—15	—
2	30	80	—	72	24	35—40	15
3	50	80	—	72	28	35—40	23
4	60	80	—	48	30	25—30	43
5	60	80	—	60	30	30—35	45
6	60	80	—	72	30	35—40	34
7	65	80	—	72	30	50—55	12
8	70	80	—	36	24	16—25	19
9	60	50	30	48	12	20—25	45
10	60	50	30	60	12	35—40	52
11	60	40	40	69	12	40—45	41
12	60	60	20	72	12	35—40	66

1 Law, loc. cit; Schepss, loc. cit.
2 These memoirs, **11**, 407 (1928)

pressure. The portion distilled off at $93° - 94°$ was found to boil at $189° - 190°$ at the ordinary pressure and to crystallize in needles. The results of analysis were:

0.2347 gm. substance gave 0.6637 g CO_2 and 0.1545 g H_2O,

$C = 77.13 \%$, $H = 7.36 \%$; Calc. $C = 77.78 \%$, $H = 7.41 \%$.

The relation between its yield and the conditions for electrolysis is shown in Table II.

From the table it is seen that the reduction must be conducted at $30° - 40°$ using a cathode solution consisting of 60% sulphuric acid. The effect of alcohol on the electrolysis is similar to that in the case of anisaldehyde.

3. p-Oxybenzaldehyde

Schepss[1] succeeded in reducing it to p-cresol with 41% yield. Using the zinc amalgam cathode I obtained a far better result. The reduction-product was subjected to fractional distillation under the reduced pressure of 18 mm. and the portion coming off at $95° - 100°$ was collected, and it was purified by again distilling. It boiled at $200° - 202°$, and gave the following results when analysed,

0.1837 gm. substance gave 0.5226 g CO_2 and 0.1215 g H_2O,

$C = 77.79 \%$, $H = 7.40 \%$; Calc. $C = 77.78 \%$, $H = 7.41 \%$.

The reduction of this aldehyde is badly effected by alcohol, so that the presence of alcohol in the cathode solution must always be avoided (see Table III).

Table III

No.	Catholyte		Current density amp./100 sq. cm.	Current quantity amp.-hour	Temperature °C	p-Cresol %
	60% sulphuric acid cc	Alcohol cc				
1	40	40	72	12	$38 - 42$	14
2	50	30	48	12	$23 - 26$	20
3	60	20	72	12	$35 - 40$	27
4	80	—	72	24	$35 - 40$	58

1 Loc. cit.

4. Vanillin

Law[1] could obtain no reduction products by electrolyzing vanillin in an alcohoric sulphuric acid solution with the cathode of copper or nickel, while Schepss[2] obtained creosol with 28 % yield by using a cadmium cathode.   I took a sulphuric acid solution containing no alcohol as the cathode solution, to which vanillin was added in suspension.   The electrolysis was carried out with the zinc amalgam cathode, the cathode solution being vigorously agitated.   Creosol isolated in the usual way was found to boil at $219°-221°$.

0.1711 gm. substance gave 0.4345 g CO_2 and 0.1114 g H_2O,

$C=69.26$ %, $H=7.28$ % ;   Calc. $C=69.56$ %, $H=7.25$ %.

In the experiment, the results of which are shown in the next table, 80 cc. of sulphuric acid of different concentrations was used in each case.

Table   IV

No.	Sulphuric acid %	Current density amp./100 sq. cm.	Current quantity amp. hour	Temperature °C	Creosol %
1	20	60	20	45—50	40
2	30	60	20	40—45	51
3	40	60	20	45—50	46
4	40	60	25	25—30	49
5	50	42	25	20—25	51
6	50	72	28	35—40	73
7	60	72	28	35—40	75
8	60	72	28	45—50	68

The influence of the concentration of sulphuric acid is, in this case, not so considerable, though $50-60$ % acid gave the best result. Temperature also does not much influence the reduction-reaction ; at the lower temperatures the material yield was increased but the current efficiency was greatly decreased.

To see the influence of alcohol on the reduction of vanillin 50 cc. of 60 % sulphuric acid mixed with 30 cc. of alcohol was taken as the cathode solution, and electrolysis was conducted at $8°-10°$ with a current

1 Loc. cit.

2 Loc. cit.

having the density of 24 amp./100 sq. cm.   As there was produced no creosol, the electrolysis was repeated with less concenrated sulphuric acid (35 %), greater current density (72 amp./100 sq. cm.) and higher temperature ($40°-42°$).   Though creosol was thus obtained, the yield was not more than 16.5 %.   How greatly alcohol interferes the progress of reduction of vanillin will be clear, when this is compared with the results given in No. 2 or No. 3 of Table IV.

5.   Piperonal

It was reported in the previous communication[1] that piperonal can be reduced to piperonyl alcohol with 90 % yield, when it is electrolyzed in a neutral solution with a mercury cathode.   Now the complete reduction of the aldehyde was undertaken by electrolyzing it in a sulphuric acid solution with a cathode of zinc amalgam.   The reduction-product was extracted with ether and purified by fractional distillation.   The portion boiling at $193°-194°$ was collected and analysed.

0.1974 gm. substance gave 0.5082 g CO_2 and 0.1075 g H_2O,

$C = 70.21$ %, $H = 6.09$ % ;   Calc. $C = 70.59$ %, $H = 5.88$ %.

The yield was, in the best case, 55 %, while Schepss[2] obtained 33 % yield by using cadmium as the cathode.

In the reduction of piperonal the presence of alcohol was found favourable, as is seen in the following table :

Table   V

No.	Catholyte		Current density	Current quantity	Temperature	Homobrenzcatechin methylene ether
	60% sulphuric acid cc	Alcohol cc	amp./100 sq. cm.	amp.-hour	°C	%
1	80	---	60	30	30 — 35	31
2	80	—	72	28	48 — 50	29
3	50	30	24	13	5 — 10	33
4	50	30	60	16	35 — 40	53
5	50	30	72	12	35 — 40	55
6	60	20	72	12	35 — 40	40
7	70	10	30	20	12 — 18	27

In conclusion, I desire to express my warm thanks to Professor M. Matsui for his constant interest and encouragement throughout the work.

1   G. Shima, these memoirs, 11, 425 (1928).
2   Loc. cit.