On the Electrolytic Reduction of Aldehydes. Part I. Formaldehyde and Acetaldehyde.

By

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ABSTRACT.

The electrolytic reduction of form and acet-aldehyde in an acid and an alkaline solution was studied with the object of learning the difference in their cathodic reactions. On comparing the various influences exercised by electrode materials, current density, temperature, concentration of acid, etc., it was found that though both aldehydes give the corresponding alcohol as the chief reduction product, formaldehyde is reducible with greater difficulty, the current efficiency for its reduction to methylalcohol being only 50%, while that for the reduction of acetaldehyde into ethylalcohol is 75%. It was also found that the presence of a great quantity of aldehydes in the cathode solution greatly lowers the yield of alcohols, as the aldehydes undergo polymerization, and change into resinous matter at the cathode. The most favourable conditions for the formation of alcohol from acetaldehyde were established.

As is well known the electrolytic reduction of the carbonyl group takes place in three different ways as shown below:

$$\begin{array}{l} \text{C=O} \\ \text{C=O} \end{array} + 2\text{H} = \begin{array}{l} \text{CHOH} \\ \text{CHOH} \end{array}$$

$$\begin{array}{l} \text{C=O} \\ \text{C=O} \end{array} + 2\text{H} = \begin{array}{l} \text{C(OH)} \\ \text{C(OH)} \end{array}$$

$$\begin{array}{l} \text{C=O} \\ \text{C=O} \end{array} + 4\text{H} = \begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array} + 2\text{H}_2\text{O}$$

The way in which the reaction proceeds chiefly depends on the

conditions of reduction on the one hand, and on the properties of tthe radicals which combine with the carbonyl group on the other. About the latter relation, as no generalization is yet established the author attempted this investigation with the object of contributing something toward it.

Formaldehyde and acetaldehyde were selected as simple carbonyl compounds, and their cathodic behavior was thoroughly studied.

Formaldehyde

As commercial formalin was found to contain about 12% of methyl alcohol besides 35% of formaldehyde it was treated with conc. sulphuric acid to transform the aldehyde into the para-variety, and paraformaldehyde precipitated as a white powder after having been well washed and dried was heated to decompose it again to simple formaldehyde which was dissolved in water and used in the experiment. The presence of methyl alcohol, however, does not interfere with the progress of the cathodic reduction, and so we may use formalin without purifying it, if we previously determine the exact quantities of methylalcohol and of the formaldehyde which are contained in it.

The method of Seyewetz and Baden[1] for determing formaldehyde, and also that of Bamberger[2] for estimating methylalcohol, in formalin were found simple and accurate.

Preliminary Experiment

A porous cell containing 8·7 grms of formaldehyde, 100 c.c. of water, 40 c.c. of 50% sulphuric acid, and a lead cathode (plate of 75 sq. cm.) was tightly stoppered with a cork carrying a reflux condenser. It was dipped in the anode solution consisting of dil. sulphuric acid (1·12) and used as the cathode compartment. As the anode platinum was taken. Keeping the temperature of the bath at 18°—20° by cooling it with running water, a current of 5 amperes was passed for 2·5 hours.

After electrolysis a white turbidity which was formed in the cathode solution was precipitated by means of a centrifugal machine, and the formaldehyde still remaining unchanged and the methylalcohol formed by reduction were determined by the methods of Seyewetz and Baden and of Zeisel respectively. The amount of formaldehyde remaining unchanged was found to be 4·23 grms and that of the methylalcohol produced to be 2·906 grms, from which the material yield and the current efficiency

1 J. Soc. Chem. Ind., **25**, 202 (1906).
2 J. Ang. Chem., **17**, 1246 (1904).

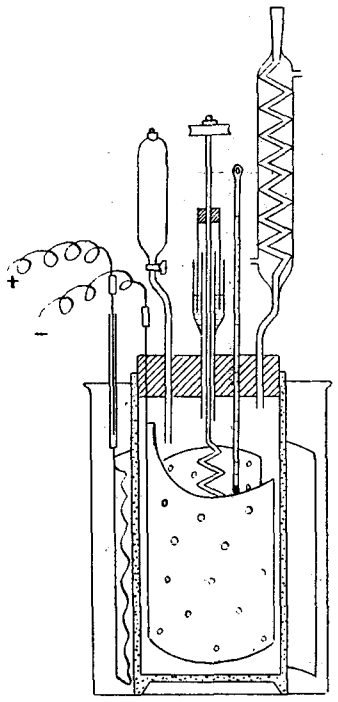
are calculated to be 60·54% and 38·90% respectively.

A similar experiment was next carried out using a copper electrolytically coated with cadmium as the cathode. A current of 3 amperes was passed for 5 hours at 19°, and the gas evolved from the cathode was collected and analysed. It was found that while 7 grms of formaldehyde were reduced, about 158 c.c. of methane were evolved, that is, the material yield for methane was 2·8%.

Quantitative Investigation

The general aspect of the reduction having been made clear in the preliminary experiment, a quantitative investigation was then undertaken in order to learn the influence exercised by current density, electrode material, concentration of acid or alkali in the cathode solution, etc., upon the reduction,

Fig. 1.



The apparatus used for the experiment is shown in the accompanying figure. The porous cell used as the cathode compartment was provided with a cathode, a stirrer, a thermometer, a dropping funnel and a reflux condenser, and tightly closed.

The solution after electrolysis, was treated in the same manner as in the preliminary experiment, and the methyl alcohol formed was estimated by measuring its specific gravity at 25°.

1. *Influence of Current Density*

(a) Alkaline solution

Cathode solution : 100 c.c. of 5% NaOH + 8·6 grms CH_2O.

Anode solution : 5% NaOH, Cathode : Copper plate of 75 sq. cm.

Anode : Platinum. Temperature : 15°—20°

Current quantity : 15 amp-hours.

Table I.

Current density (amp/100 sq. cm.)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
1·3	6.04	71	67
2·0	6.06	74	72
3·3	6.51	81	73
4·0	6.35	79	71
4·7	6.08	79	73

(b) Sulphuric acid solution

Cathode solution : 100 c.c. of H_2SO_4(1·12)+8·6 grms CH_2O.
Anode solution : H_2SO_4(1·12). Cathode : Pb of 68·8 sq. cm.
Anode : Pt. Temperature : 10°—12°.

Table II.

Current density (amp/100 sq. cm.)	Current quantity (amp-hour)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
1·5	17·2	3.86	63	38
2·2	22·5	6.68	81	50
2·9	23·7	7·47	89	53
3·6	22·5	7·01	89	52
4·4	18·0	5·12	84	48
5 1	23·0	6.09	82	44

3·0—3·5 amperes per 100 sq. cm. were thus shown to be the most suitable current density.

2. Influence of the Concentration of Alkali

The conditions under which the electrolysis was carried out were exactly the same as in (1), (a).

Table III.

Conc. of alkali (%)	Current quantity (amp-hour)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
2	12.5	5·23	69	70
4	15·0	6·51	81	73
8	15·0	4 09	64	46

The most favourable concentration of alkali was thus found to be 4%.

In order to trace the progress of reduction, the hydrogen used up for reduction was calculated by measuring the volume of gases liberated

in every one minute period from the cathode and from a detonating gas voltameter placed in the same circuit. The result is represented in the following diagram:

Fig. 2.

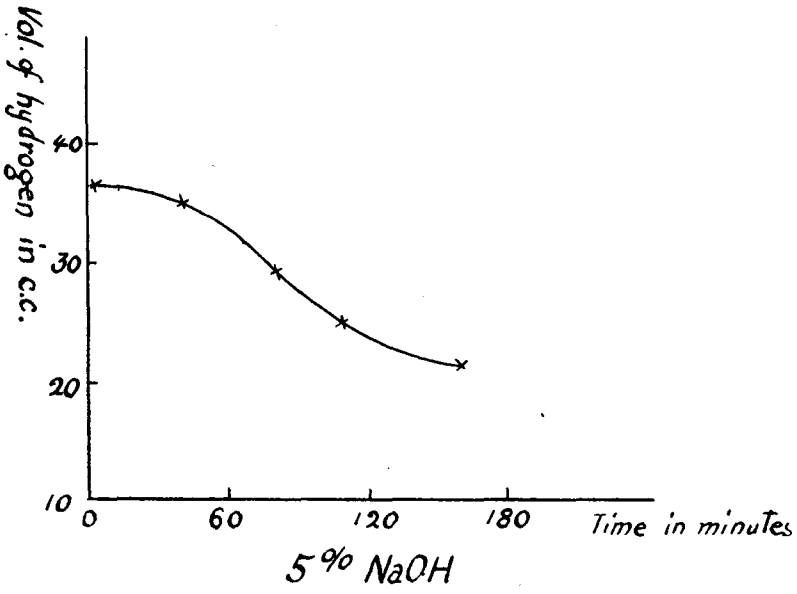
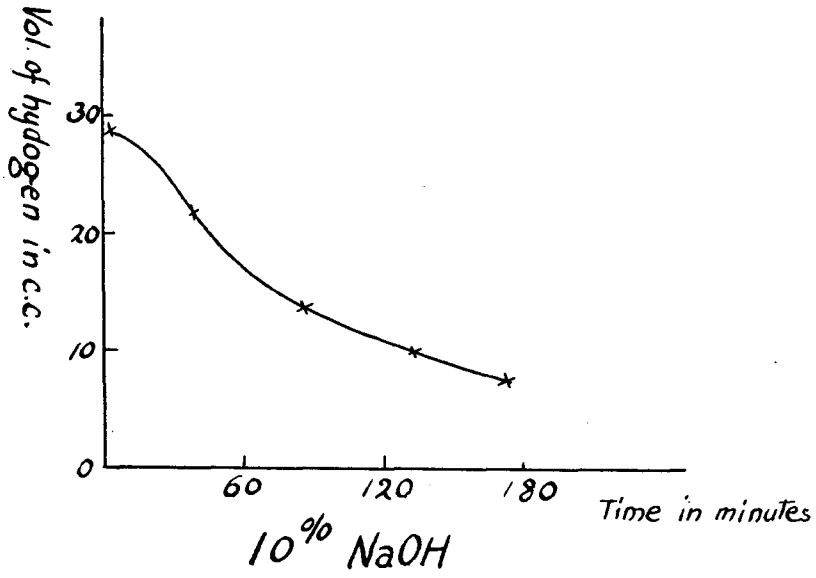


Fig. 3.



3. Influence of Cathode Material

(a) In an alkaline solution

Cathode solution : 100 c.c. of 2·5% NaOH + 8·6 grms CH_2O
Current density : 3·3 amp/100 sq. cm.
Other conditions were the same as in (1).

Table IV.

Cathode	Current quantity (amp-hour)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
Zn	14·2	7·15	83	84
Cu	12·5	5·23	69	70
Pb	12·5	4·10	50	55
Ni	12·5	4·35	9	5

(b) In a sulphuric acid solution

Cathode solution : 100 c.c. of H_2SO_4 (1.075) + 8.6 grms CH_2O
Current density : 3 amp/100 sq. cm.

Table V.

Cathode	Current quantity (amp-hour)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
Pb	19·9	6·27	90	53
Hg	23·5	0·87	20	6
Cd	20·3	6·52	88	54
Sn	23·0	0·46	24	3

In either case the reducing power of the cathode materials is not parallel with their overvoltage, contradictory to the fact which is generally observed in most electrochemical reductions. Moreover, the influence of the cathode material in an acid solution greatly differs from that in an alkaline solution. It is to be noted that zinc and cadmium act most effectively, the one in an alkaline solution and the other in an acid solution.

4. Influence of Temperature

Cathode : Pb plate of 75 sq. cm. Current density : 3 amp/100 sq. cm.
Other conditions were the same as in (1), (b).

Table VI.

Temperature	Current quantity (amp-hour)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
5°—10°	18.0	4.41	91	41
10°—15°	19.9	6.27	90	53
26°—43°	18.0	7.46	86	69

With the rise of temperature, though the current efficiency increases the material yield decreases, thus making a moderate temperature such as 10°–15° the most suitable for the reduction.

5. *Influence of the Concentration of Sulphuric Acid*

Cathode solution: 100 c.c. of sulphuric acid + 8·7 grms CH_2O
Current density: 3 amp/100 sq. cm.
Other conditions were the same as in (1), (b).

Table VII.

Density of H_2SO_4	Current quantity (amp-hour)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
1·035	19·7	4·96	90	42
1·075	19·9	6·27	90	53
1·120	22·3	6·70	89	50
1·170	24·0	6·89	86	48
1·280	20·3	4·79	80	39

The progress of the reduction, traced in the same manner as described before, is represented in Fig. 4—Fig. 8.

6. *Influence of the Concentration of Formaldehyde*

Cathode solution: 100 c.c. of formaldehyde solution + 25c.c. of H_2SO_4 (1·315).
Temperature: 10°–15°. Other conditions were similar to those in (4).

Table VIII.

Formaldehyde taken (grm)	Current quantity (amp-hour)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
8·72	19·9	6·27	90	53
17·63	40·5	12·28	81	51
26·45	54·0	15·36	71	48
35·25	81·0	22·91	62	47

From this table it is seen that both the material yield and the current efficiency decrease when the concentration of aldehyde increases. Probably this is due to the polymerization which the formaldehyde undergoes bofore it is reduced.

To avoid a high concentration of formaldehyde in the cathode solution, a reduction experiment was conducted by adding formalin from time to time, instead of adding the whole quantity at the commencement of reduction, and by this means a very satisfactory result was obtained as is shown below:

Cathode solution: 10 % sulphuric acid solution to which a formalin solution was gradually added so as to keep the concentration of formaldehyde always near 5%.

Current quantity: 63 amp-hours. Temperature: 20°–25°.

Other conditions were exactly the same as in (6).

Table IX.

Total formaldehyde (grm)	CH_3OH formed (grm)	Material yield (%)	Current efficiency (%)
25·98	19·63	85	52

Fig. 1.

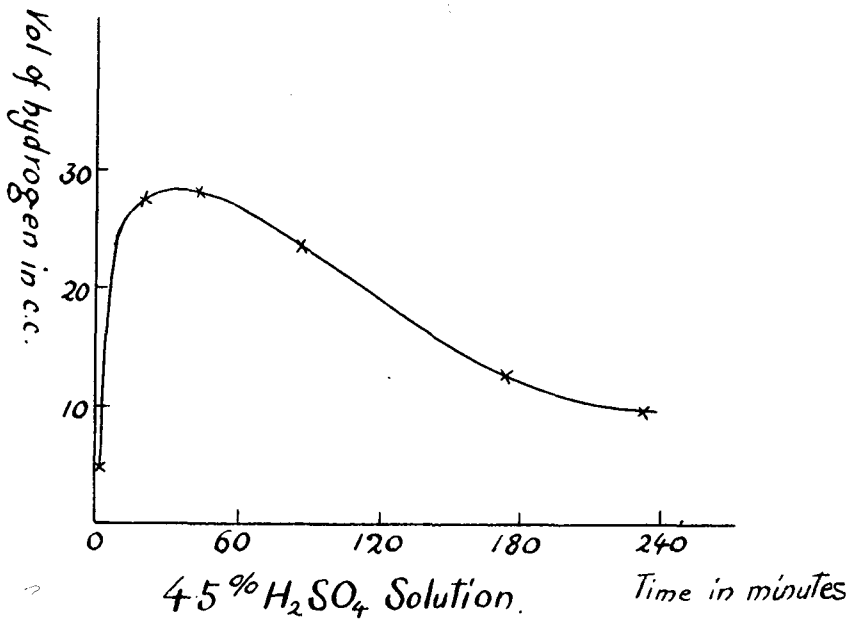


Fig. 5.

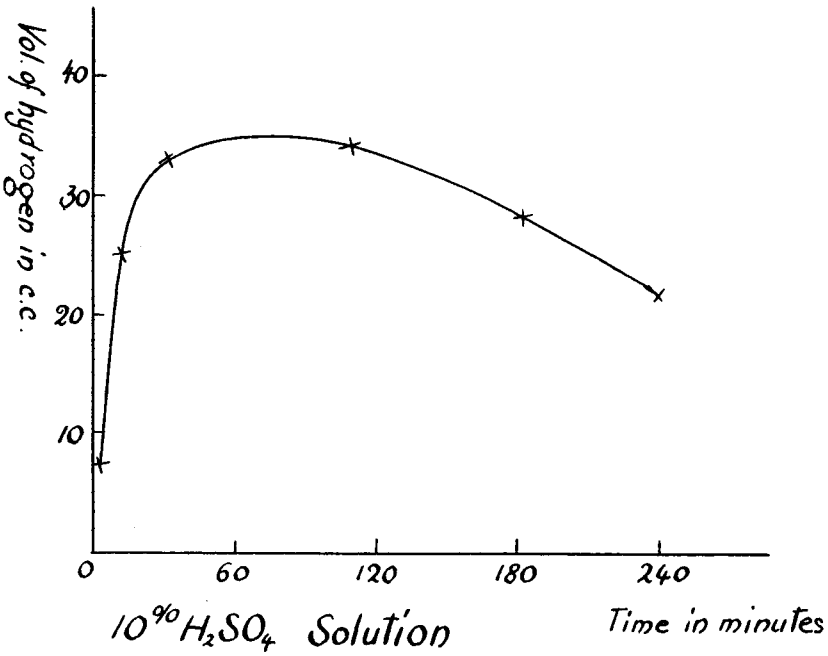

Vol. of hydrogen in c.c.
40
30
20
10
0
60
120
180
240
10% H_2SO_4 Solution
Time in minutes

Fig. 6.

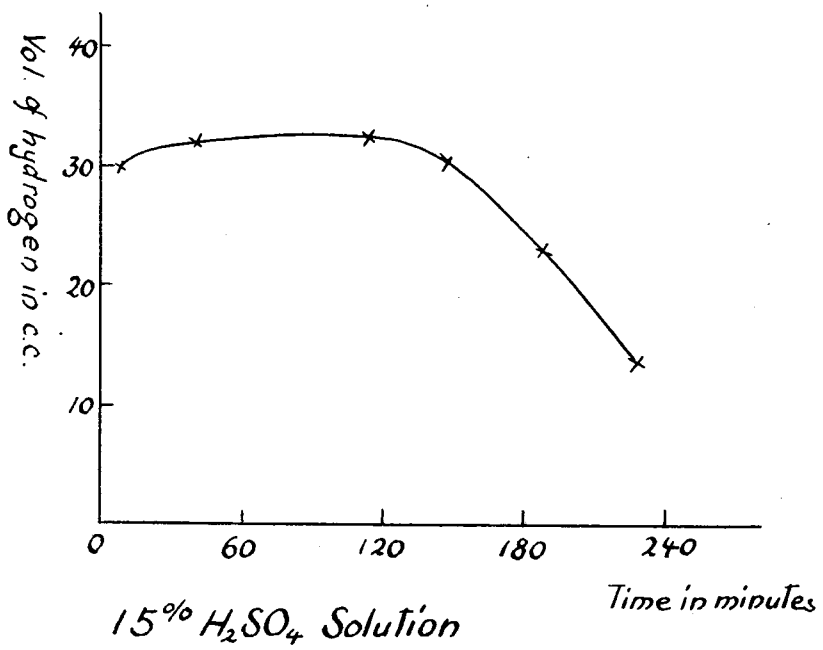

Vol. of hydrogen in c.c.
40
30
20
10
0
60
120
180
240
Time in minutes
15% H_2SO_4 Solution

Fig. 7.

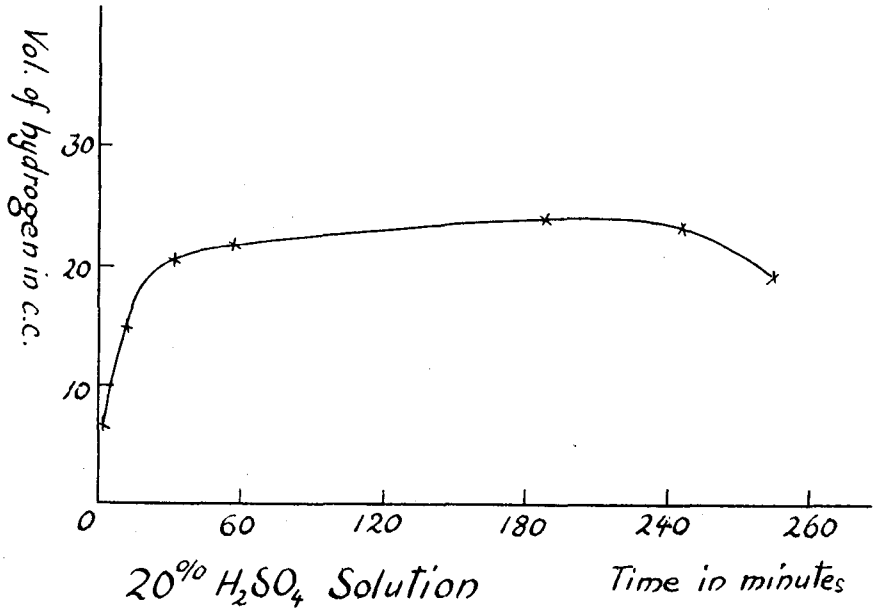
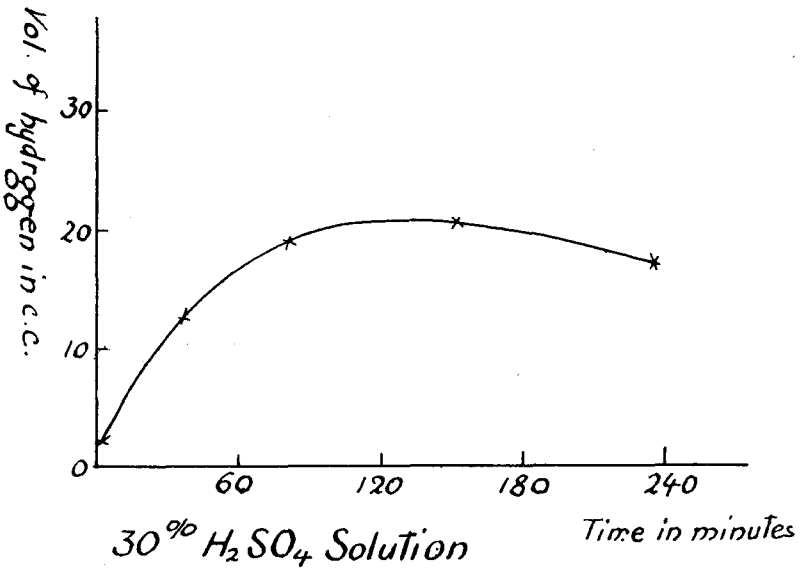

Vol. of hydrogen in c.c.
30
20
10
0
60
120
180
240
260
20% H_2SO_4 Solution
Time in minutes

Fig. 8.


Vol. of hydrogen in c.c.
30
20
10
0
60
120
180
240
30% H_2SO_4 Solution
Time in minutes

Acetaldehyde[1]

The apparatus used in the experiment and the treatment of the cathode solution after electrolysis were similar to those employed for the reduction of formaldehyde.

1. Influence of Current Density

Cathode solution: 50 c.c. of 5% H_2SO_4 + 50 c.c. of about 60% aldehyde solution.

Cathode: Pb. Anode: Pt.

Anode solution: 10% H_2SO_4

Current quantity: 9–10 amp–hours. Temperature: 8°–12°

Table I.

Current density (amp/100 sq. cm.)	Aldehyde reduced (grm)	Material yield (%)	Current efficiency (%)
2·2	5·94	69	50
3·0	6·83	72	57
3·7	5·77	85	69
4·5	5·72	81	66
5·9	5·66	77	58

The current of 3·5–4·0 amp/100 sq. cm. gave the best yield.

2. Influence of Temperature

Current density: 3·71 amp/100 sq. cm.

Other conditions were maintained the same as in (1).

Table II.

Temperature	Aldehyde reduced (grm)	Material yield (%)	Current efficiency (%)
4°—7°	7·04	84	69
8°—22°	7·05	85	73
25°—40°	6·76	72	70

A temperature near 20° is thus shown as the most favourable.

1 While the work was in progress Mr. T. Sumiya's paper treating of the same subject was published by the Osaka Technical Research Institute.

3. Influence of the Concentration of Sulphuric acid

Cathode solution: A sulphuric acid solution containing 50 c.c. of about 60% aldehyde solution.

Temperature: 18°–21°. Other conditions were the same as in (2).

Table III.

H_2SO_4 in catholyte (%)	Aldehyde reduced (grm)	Material yield (%)	Current efficiency (%)
60	6.74	74	69
50	6.71	77	70
30	6.45	82	72
20	8.55	88	79
5	7.05	85	73

The most suitable concentration of sulphuric acid was found to be 10–15%.

4. Influence of Cathode Material

Cathode solution: 50 c.c. of 5% H_2SO_4 + 50 c.c. of about 60% aldehyde solution.

Current quantity: 10 amp-hours.

Other conditions were exactly the same as those in (3).

Table IV.

Cathode material	Aldehyde reduced (grm)	Material yield (%)	Current efficiency (%)
Pb	7.05	85	74
Cu	3.30	40	15
Fe	2.31	36	10

Lead was thus found to give the best results.

5. Influence of the Concentration of Aldehyde

Cathode solution: 50 c.c. of 20% H_2SO_4 + 50 c.c. of aldehyde solution.

Other conditions were the same as in (3).

Table V.

Aldehyde[1] (grm)	Current quantity (amp-hour)	Material yield (%)	Current efficiency (%)
9·09	10·3	88	79
15·84	20·0	69	59
25·08	30·0	57	47
30·62	45·0	39	29

The presence of a great quantity of acetaldehyde in the cathode solution was found to be very unfavourable to reduce it to alcohol as was also observed in the case of formaldehyde.

When we compare the results so far obtained it may be seen that, while formaldehyde and acetaldehyde can be reduced to the corresponding alcohol with a good material yield amounting to 80-90%, the current efficiency for the reduction of formaldehyde is far lower than that for the reduction of acetaldehyde, the former being only 52% against 80% of the latter. This evidently shows that formaldehyde is a worse depolarizer than acetaldehyde, and this relation is also shown by their behavior toward the copper electrode with which the former is hardly reducible, while the latter is transformed into ethylalcohol with a 40% current yield.

The difference existing between the cathodic reactions of different carbonyl compounds is still manifest when we compare these aliphatic aldehydes with the aromatic. Benzaldehyde, for example, is easily reduced into hydrobenzoin both in an acid and an alkaline solution, and is also reducible even to a hydrocarbon with a cathode of moderate overvoltage such as copper.

The condition most favourable for the preparation of alcohol from acetaldehyde

Nowadays when acetaldehyde can conveniently be prepared from acetylene, the reduction of acetaldehyde may afford the possibility of producing alcohol technically in case of need. It will not therefore be superfluous to describe here the best conditions under which the electrochemical reduction of acetaldehyde is to be carried out.

The electrolysis should be conducted with a cathode solution contain-

1 In this table the amount of acetaldehyde which present in the cathode solution at the commencement of reduction is given.

ing about 10–15% of sulphuric acid by passing a current of 3.5–4 amperes per 100 sq. cm. at a temperature near 20°. As the cathode, lead is most suitable, and the aldehyde should be added gradually into the cathode solution at such a rate as to keep the concentration of it always near 5%. The material yield amounts to 85%, and the current efficiency 75%.

The author takes this opportunity of warmly thanking Professor M. Matsui at whose suggestion the work was performed.