

On the Mechanism of Kolbe's Reaction, Part I. Electrolysis of Free Acetic Acid.

By

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Nearly 100 years have elapsed since Kolbe first found out that salts of a fatty acid, when electrolysed, generally undergo such a change that they produce hydrocarbon, alcohol or ester at the anode. During this rather long period, though several theories have been advanced to explain the mechanism of the famous reaction, the question still remains not entirely settled. Kolbe¹ himself considered it to be a simple anodic oxidation, while Brown and Walker² regarded the anodic discharge of anions as the essential cause of the reaction. A few years ago, Fichter³ summarized his own works as well as those of other authors on this subject, and arrived at the conclusion that Kolbe's reaction is no other than simple oxidation of a free fatty acid which becomes liberated at the anode on electrolysis of its salts. Recently, R. Matsuda⁴ also published the results of his experiments, in which Kolbe's reaction was shown to be always accompanied by the formation of some peroxidic substances, and endorsed Fichter's view throughout. As to the intermediate formation of peroxidic compounds, such as alkyl peroxide and peracid, there seems to remain no room to doubt it; but the simple oxidation theory cannot be accepted without hesitation, as evidences contradictory to the theory are many, while those supporting it are rather scanty.

With the object of finding some decisive evidence for or against

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1. *Ann.*, **69**, 279 (1859).
 2. *Ann.*, **261**, 107 (1891).
 3. *J. chem. Ind.*, 1929, *Tr.* **48**, 347, 354.
 4. *Bull. chem. Soc. (Japan)*, **7**, 18, 297 (1932).

the "Discharge Theory", electrolysis of free fatty acids was undertaken by the present authors. The work on the electrolysis of acetic acid here communicated constitutes the first report; it will shortly be followed by others treating of the electrolytical behavior of higher fatty acids now being studied.

As will be seen in the experimental part of this report, acetic acid evolves ethane gas when electrolysed at 15° with a current of 0.071 Amp/sq. cm., even in such a dilute solution as 5%. The amount of the gas evolved becomes more significant as the concentration of the acid is increased and attains its maximum at the concentration of 30%. From this point, the more concentrated the acid is, the less ethane is evolved. At the maximum point the ratio of the volume of ethane to that of hydrogen was found to be about 0.75. These relations can be understood from the stand-point of the discharge theory, but not from that of the simple oxidation theory, to which the above facts stand in direct opposition.

Addition of a strong acid such as sulphuric acid greatly hinders the evolution of ethane. As little as 0.1 c.c. of concentrated sulphuric acid (95.6%) is quite sufficient entirely to prevent the formation of ethane in 250 c.c. of 20% acetic acid. Phosphoric acid, oxalic acid and formic acid also act similarly though not so strongly. That the degree of dissociation of acetic acid had become very much depressed at the point at which the evolution of ethane entirely stopped or much decreased, is clearly shown by the lowering of the pH value simultaneously observed. An acid feebler than acetic acid, as for example, boric acid produces no appreciable disturbance of the reaction, as it exerts no influence on the dissociation of acetic acid, and the pH value of the solution remains constant at 2.2. A strong indifferent electrolyte, the presence of which has no effect on the degree of the dissociation of acetic acid, also prevents the progress of Kolbe's reaction. When potassium sulphate is added to 250 c.c. of 20% acetic acid, even an amount as small as 0.1 gram gives rise to a remarkable decrease in the evolution of ethane, which ceases entirely on the addition of 1 gram. Of course, such an electrolyte as potassium sulphate has nothing to do with the degree of dissociation of acetic acid, and consequently, the pH value of the solution is not altered by its addition. But the discharge of acetate ions becomes more and more difficult when the concentration of other electrolytes, especially those of high conductivity, is increased, till at last the concentration of discharged

acetate ions becomes so small that they can not enter into polymerization to form acetyl peroxide. The reason why a very dilute solution does not undergo Kolbe's reaction, will be understood by analogy.

The influence of monohydrogen sodium phosphate, dihydrogen sodium phosphate, normal sodium phosphate, sodium borate, sodium oxalate and sodium formate was also examined. The results always confirmed the above view.

Experimental

Electrolysis was conducted in a bath of about 250 c.c. capacity without any diaphragm. As the cathode, a platinum plate (5×7 cms.) and as the anode, a platinum wire having a surface area of 4.24 sq. cms. were used. The bath was stoppered by a cork carrying two delivery tubes besides the electrodes. One of these served as the delivery tube for the gases formed, and the other, in the form of a syphon, as that for the electrolytic solution, which was taken out at intervals for determination of its pH value. The indicators used for the pH determination were as follows:

	pH
Methyl violet	0.1 - 3.2
Tropæolin O O	1.3 - 3.0
Methyl orange	3 - 4.4
Methyl red	4.4 - 6.0
Bromcresol purple	5.3 - 6.8
Phenol red	6.8 - 8.4

The apparatus was placed in a large vessel into which a current of water was always passed. In every case 50 c.c. of evolved gas were collected when 5 minutes elapsed after the commencement of the electrolysis.

1. Electrolysis of Acetic Acid Alone

Experiment 1.—Acetic acid of various concentration was electrolysed at 15° with a current of 0.071 Amp/sq. cm. The results are shown in Table I.

Kolbe's reaction was observed to take place slightly with 5 % acetic acid and to become gradually more marked as the acid concentration was increased, reaching the maximum with 30 % acetic acid. When the concentration was more than 60 %, the passage of the

electricity through the acetic acid solution became more and more difficult, and at the same time the evolution of ethane became less and less.

Table I

%	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
5	0.9	31.1	—	3.6	64.4	0.056	2.4
6	10.4	19.3	—	11.3	58.0	0.195	2.4
7	14.2	12.6	—	16.2	56.0	0.289	2.35
8	21.9	4.6	0.5	25.3	47.7	0.533	2.35
10	22.5	2.8	0.5	27.6	46.6	0.592	2.3
15	24.2	2.1	0.5	29.8	43.2	0.687	2.2
20	26.3	1.5	0.7	30.6	40.9	0.748	"
30	25.6	0.7	0.9	30.8	42.0	0.734	"
40	25.8	1.2	2.3	30.3	40.4	0.749	"
60	18.1	3.4	0.7	25.5	52.3	0.484	"

II. Influence of Temperature and Current Density

Experiment 2.—The influence of temperature was first examined under exactly the same conditions as in Experiment 1, and the following results were obtained:

Table II

Temp.	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
15°	26.3	1.5	0.7	30.6	40.9	0.748	2.2
25°	29.8	1.5	0.7	26.9	41.1	0.656	"
35°	29.7	2.7	0.7	24.9	42.0	0.590	"
45°	38.2	2.2	0.6	21.3	37.7	0.565	"

Though the pH value of the solution remained always at 2.2, the evolution of ethane became less and less as the temperature was raised. This is perhaps due to the facts that on the one hand high temperature is unfavorable to the formation of intermediate peroxidic substances, and on the other, it promotes complete oxidation of acetic acid.

Experiment 3.—The influence of current density was then studied under the same conditions as in the foregoing experiments. As was expected, high density was found to favor Kolbe's reaction. The results are shown in Table III.

III. Influence of Acids Stronger than Acetic Acid

Experiment 4.—In order to discover what effect sulphuric acid has on the electrolysis, concentrated (95.6%) sulphuric acid was added to 250 c.c. of 20% acetic acid, and the mixture was electrolysed under the same conditions as those used in experiment 1. The results are shown in Table IV.

Table III

Amp/sq. cm.	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0.142	35.4	0.7	0.4	27.7	35.8	0.769	2.2
0.071	26.4	1.5	0.7	30.6	40.9	0.748	„
0.047	24.0	2.5	1.1	27.9	44.5	0.626	„
0.023	19.0	2.3	0.6	28.7	48.5	0.592	„

Table IV

H ₂ SO ₄ c.c.	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.02	18.5	1.9	3.0	15.7	60.9	0.258	2.1
0.1	7.7	8.3	3.0	—	81.0	—	1.8

Experiment 5.—The influence of phosphoric acid was next examined by adding 61% phosphoric acid to 250 c.c. of 20% acetic acid and electrolysing under the same conditions as in Experiment IV. The results are shown in Table V.

Table V

H ₃ PO ₄ c.c.	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.25	19.7	4.1	1.3	15.5	59.4	0.261	2.05
1	6.6	17.9	1.1	3.2	71.2	0.045	2.0
2	3.9	23.7	1.1	—	71.3	—	1.7

Experiment 6.—Varying quantities of oxalic acid were added to 250 c.c. of 20 % acetic acid, and their influence was investigated by electrolysing the solution under the same conditions as in the above experiment. The results shown in Table VI were obtained. The retarding action of oxalic acid is comparatively small and becomes gradually less as the electrolysis progresses, as is seen in Table VII. This is evidently due to the fact that the oxalic acid is gradually lost by anodic oxidation.

Table VI

$C_2O_4H_2 \cdot 2H_2O$ (gms.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.2	24.9	1.3	1.8	28.2	43.8	0.644	„
0.5	26.7	1.1	0.8	25.9	45.5	0.569	2.1
0.7	27.7	1.6	0.6	24.3	45.8	0.518	2.0
1	27.7	1.6	0.4	23.2	47.1	0.493	1.9
2	28.0	1.9	0.6	16.1	53.4	0.302	1.7
3	29.2	1.3	0.4	10.9	58.2	0.187	1.65
5	36.9	3.5	0.2	0.9	58.5	0.015	1.55

Table VII

To 250 c.c. of 20 % acetic acid 3 grams of oxalic acid were added.

Time (Mins)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
5	29.2	1.3	0.4	10.9	58.2	0.187	1.65
30	58.3	1.1	0.5	6.9	33.3	0.207	1.7
60	60.3	0.7	0.7	8.2	30.1	0.272	1.75
120	55.9	0.7	0.4	12.4	30.6	0.405	1.85
240	51.9	0.8	0.4	18.8	28.1	0.669	2.1

Experiment 7.—In this experiment, which was undertaken to find the influence of acid oxalate, the dissociation constant of which is nearly of the same order as that of acetic acid, results very similar to those found in experiment 6 were obtained, except that the pH of the solution gradually began to increase after 30 minutes's electrolysis (see Tables VIII and IX).

Table VIII

KHC ₂ O ₄ (gms.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.5	29.8	1.5	1.1	25.1	42.5	0.605	"
1	30.4	1.5	1.0	19.9	48.2	0.413	"
3	35.1	1.3	0.9	7.4	54.7	0.135	"
5	35.3	1.2	1.2	2.7	59.6	0.045	"

Table IX

Three grams of KHC₂O₄ were added to 250 c.c. of 20% acetic acid.

Time (mins.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
5	35.1	1.3	0.9	7.4	54.7	0.135	2.2
30	57.5	0.8	0.4	7.1	34.2	0.208	2.3
60	58.2	0.7	0.4	8.4	32.3	0.261	2.4
120	54.9	0.4	0.2	12.9	31.6	0.408	2.6
240	50.4	0.8	0.2	19.4	29.2	0.647	2.8

Experiment 8.—The influence of formic acid was then examined by adding a 95 % solution of it to 250 c.c. of 20 % acetic acid. The results are tabulated in Table X.

IV. Influence of Neutral Salts

In order to see how Kolbe's reaction of acetic acid is affected by neutral salts, the influence exerted by potassium sulphate, sodium phosphate, borax, potassium oxalate and sodium formate was studied by adding varying quantities of them to 250 c.c. of 20 % acetic acid. The results are shown in Tables XI-XV.

Table X

H ₂ CO ₂ (c.c.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
1	26.2	0.9	0.6	26.2	46.1	0.568	2.1
3	24.9	1.1	—	17.4	56.6	0.307	2.1
5	21.2	2.4	—	11.2	65.2	0.172	2.0
10	21.0	2.1	—	5.0	71.9	0.069	1.9
15	20.7	3.2	—	—	76.1	—	1.8

Table XI

K_2SO_4 (gms.)	CO_2	O_2	CO	C_2H_6	H_2	C_2H_6/H_2	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.1	9.6	5.8	2.9	4.2	77.5	0.054	"
0.2	9.8	6.3	2.9	3.7	77.3	0.049	"
0.5	9.2	6.6	2.8	3.4	78.0	0.044	"
1.0	7.5	10.4	—	—	82.1	—	"

Table XII

$Na_3PO_4 \cdot 12H_2O$ (gms.)	CO_2	O_2	CO	C_2H_6	H_2	C_2H_6/H_2	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.1	20.2	1.8	1.2	17.7	59.1	0.300	2.25
0.5	20.5	1.8	1.4	17.8	58.5	0.304	2.4
1	20.9	1.2	0.8	17.8	59.3	0.300	2.7
5	20.9	1.1	1.1	16.6	60.3	0.275	3.2
10	20.7	1.9	1.3	14.8	61.3	0.242	3.5
15	21.9	2.0	1.5	14.2	60.4	0.235	3.8
25	31.1	1.4	1.1	12.2	54.2	0.224	4.0
50	42.8	2.0	0.9	7.8	46.5	0.168	4.2

Table XIII

Borax (gms.)	CO_2	O_2	CO	C_2H_6	H_2	C_2H_6/H_2	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
1	28.7	1.5	0.4	29.4	40.0	0.735	2.6
2	29.1	1.3	0.7	29.8	39.1	0.762	2.8
5	27.2	1.0	0.4	29.9	41.7	0.717	3.0
10	26.1	1.7	0.4	29.9	41.9	0.714	3.2

Table XIV

$K_2C_2O_4 \cdot H_2O$ (gms.)	CO_2	O_2	CO	C_2H_6	H_2	C_2H_6/H_2	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.5	29.7	1.7	0.8	24.7	42.1	0.587	2.3
1	32.9	0.7	0.9	22.8	42.7	0.534	2.5
3	37.1	1.2	0.4	6.7	54.6	0.123	2.7
5	39.1	1.6	0.2	2.7	56.4	0.048	2.8

Table XV

HCO ₂ Na (gms.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.5	27.6	1.4	0.7	28.2	42.3	0.662	2.4
1	28.4	1.6	—	25.2	44.8	0.562	2.7
3	35.9	1.4	—	17.0	45.7	0.372	2.9
5	39.3	0.6	—	15.6	44.5	0.350	3.2
10	49.8	1.0	—	8.7	40.5	0.215	3.4
15	53.3	0.9	—	6.0	39.8	0.151	3.6
25	63.3	0.9	—	4.2	31.5	0.133	3.8
50	60.3	0.4	—	1.7	37.6	0.045	4.0

Neutral salts of a feeble acid, such as boric acid, cause a gradual increase in the pH value, and also of acetate ions, and for this reason, the discharge of acetate ions does not become much obstructed even in the presence of large numbers of borate ions. A similar but much stronger effect was observed with monohydrogen sodium phosphate, as is seen in Table XVI.

Table XVI

Na ₂ HPO ₄ , 12H ₂ O (gms.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.1	22.4	1.6	0.8	18.1	57.1	0.317	2.25
0.5	22.0	1.7	0.8	17.6	58.9	0.295	2.3
1	21.4	1.9	1.4	14.1	61.2	0.230	2.4
5	22.4	2.3	1.3	14.0	60.0	0.233	2.8
10	22.1	2.2	1.2	14.2	60.3	0.235	3.2
15	22.0	2.5	0.9	13.8	60.8	0.227	3.5
25	23.9	2.5	0.6	13.5	59.5	0.227	3.8
50	21.3	3.6	0.7	10.6	63.8	0.166	4.0

The influence of dihydrogen sodium phosphate was observed to be much stronger, as is shown in Table XVII.

Though dihydrogen sodium phosphate is weaker acid than hydrogen potassium oxalate it has a stronger suppressive action on the evolution of ethane. The greater conductivity of the former salt probably accounts for this.

Table XVII

NaH ₂ PO ₄ , H ₂ O (gms.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
0	26.3	1.5	0.7	30.6	40.9	0.748	2.2
0.1	21.8	2.5	0.4	16.8	58.5	0.287	"
0.5	20.3	2.8	0.9	16.7	59.3	0.282	"
1	12.4	8.7	1.2	8.5	69.2	0.123	2.3
3	5.3	20.5	1.6	—	72.6	—	"

As is shown in Table VII, the action of oxalic acid to prevent the progress of Kolbe's reaction decreases when the electrolysis is continued for a long time. The same results were also observed with oxalates and formates (see Tables XVIII—XXI).

Table XVIII

Three grams of KHC₂O₄ were added to 250 c.c. of 20 % acetic acid.

Time (Mins.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
5	35.1	1.3	0.9	7.4	54.7	0.135	2.2
30	57.5	0.8	0.4	7.1	34.2	0.208	2.3
60	58.2	0.7	0.4	8.4	32.3	0.261	2.4
120	54.9	0.4	0.2	12.9	31.6	0.408	2.6
240	50.4	0.8	0.2	19.4	29.2	0.647	2.8

Table XIX

Three grams of K₂C₂O₄·H₂O were added to 250 c.c. of 20 % acetic acid.

Time (Mins.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
5	37.1	1.2	0.4	6.7	54.6	0.123	2.7
30	57.7	0.4	0.4	9.0	32.5	0.277	2.8
60	58.8	0.5	0.2	11.7	28.8	0.406	2.9
120	51.3	0.8	0.4	17.7	29.8	0.594	3.0
240	51.7	0.8	0.4	18.8	28.3	0.664	3.1

Table XX

To 250 c.c. of 20 % acetic acid 5 c.c. of 95 % formic acid were added.

Time (Mins.)	CO ₂	O ₂	CO	C ₂ H ₆	H ₂	C ₂ H ₆ /H ₂	pH
5	21.2	2.4	—	11.2	65.2	0.172	2.0
30	40.6	1.6	—	10.7	47.1	0.227	"
60	46.6	1.0	—	10.5	41.9	0.251	"
120	49.5	0.7	—	10.4	39.4	0.264	"
240	49.2	0.7	—	10.8	39.3	0.275	"

Table XXI

Five grams of NaCO_2H were added to 250 c.c. of 20 % acetic acid.

Time (Mins.)	CO_2	O_2	CO	C_2H_6	H_2	$\text{C}_2\text{H}_6/\text{H}_2$	pH
5	39.3	0.6	—	15.6	44.5	0.350	3.2
30	46.2	0.8	—	14.1	38.8	0.364	"
60	49.8	1.0	—	13.3	35.8	0.368	3.3
120	49.2	0.9	—	15.0	34.9	0.429	3.4
240	47.1	1.1	—	16.2	35.6	0.455	3.4

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