THE RELATION BETWEEN KOLBE'S REACTION AND HYDROGEN ION CONCENTRATION. VII. THE MECHANISM OF KOLBE'S REACTION.

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The present author's observation on the gas evolved from the solutions of potassium acetate under electrolysis, and the studies on chemical behaviours of the solutions during the electrolysis—especially their oxidizing and reducing actions—led him to the conclusion that ethane in these cases had its origin in acetyl peroxide, as already had been reported in the previous communication.(1)

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(1) This Bulletin, **7** (1932), 18.

In order to examine the validity of the Peroxide Theory, electrolyses of potassium propionate solutions were carried out under nearly the same principle as in the case of the acetate solutions.

Although there is a report from another source that a highly concentrated solution of sodium propionate acidified with propionic acid produces butane in a larger quantity than ethylene⁽¹⁾ such is to be regarded only as an exceptional case, since ethylene, from a general point of view, may be taken as the principal product of the Kolbe's Reaction of a propionate solution. Because a concentrated solution of potassium propionate produces ethylene in an overwhelming quantity, accompanied by far less amounts of butane and ethyl propionate; and moreover, butane decreases as the concentration of the solution is lowered.⁽²⁾

As a proper sequence the present paper chiefly deals with the relation between the ethylene formation and oxidizing action of the electrolysed solution.

As is mentioned below, propionyl peroxide which can be taken as the original product of the Kolbe's Reaction of potassium propionate just as the acetyl peroxide in the case of potassium acetate, is a substance of a greater stability than the latter,⁽³⁾ hence it follows that propionyl peroxide must be more resistible to the anodic actions than acetyl peroxide. It may be therefore presumed that there is formed, in this case, propionyl peroxide or certain peroxidic substances formed from it by decomposition, in quantities greater than equivalent to the corresponding peroxidic substances produced in the case of potassium acetate, thus giving a stronger oxidizing power to the propionate solution.

As are described below, the experimental facts observed by the author are all in the fullest agreement with this assumption, and exactly as in the case of the acetate, the formation of hydrogen peroxide is explained by assuming that it is produced by the hydrolyses of propionyl peroxide as shown in the following equations :

$$(C_2H_5COO)_2+H_2O = C_2H_5COOH+C_2H_5COOOH \quad \ldots\ldots\ldots\ldots \quad (1),$$

$$C_2H_5COOOH+H_2O = C_2H_5COOH+H_2O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

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(1) Zimmermann, Dissertation, Gieszen, 1899.

(2) Petersen, *Z. physik. Chem.*, **33** (1900), 106.

(3) Acetyl peroxide: Nef, *Ann.*, **298** (1897), 289; propionyl peroxide, Clover, Richmond, *Am. Chem. J.*, **29**, 191.

Experimental.

The apparatus used for electrolysis were the same as those mentioned in the preceding papers,(1) 100 c.c. of the electrolyte having been employed each time.

Test for hydrogen peroxide: the presence of this substance was attested by means of a titanium sulphate solution.

Potassium permanganate test: 20 c.c. of the sample solution were acidified with an excess of sulphuric acid, and titrated with n/100 potassium permanganate solution.

Potassium iodide and starch test: 20 c.c. of the sample solution were added to a potassium iodide solution, and iodine that had been set free was titrated with n/100 thiosulphate solution, using a starch solution as the indicator. When reaction was considered to have ceased, a little more potassium iodide was added to ascertain that there was no recovery of the starch-iodine colour.

Table 1.

Electrolyses of dilute solutions of potassium propionate.

Electrolyte % KPr	pH		Duration of Electrolysis	Exam. of the solution			C_2H_4
	orig.	after		H_2O_2	$\frac{n}{100}$ $KMnO_4$	KI+Starch	
0.1	6.0	6.0	12 min.	abs.	4 drops*	no reaction	0
0.3	6.1	6.1	7	,,	7	,,	,,
0.5	,,	,,	12	,,	15	,,	,,
0.7	6.2	6.3	20	,,	25	,,	,,
1.0	,,	7.9	30	pres.	70	$\frac{n}{100}$ $Na_2S_2O_3$ 29 drops	6.5%

* 25 drops = 1 c.c.

Current density was 3.6 A/dm.^{2} at the anode in the case of 0.1% solution and 10 A/dm.^{2} in other cases. Temperature ranged 9–12°C., except in the case of 0.3% solution, which was electrolysed at 17–18°C. The gas samples were collected as follows: 35 c.c. from 0.1% solution and 60 c.c. from 0.3% solution, each during the whole course of electrolysis; but from three other solutions 60 c.c. were collected in the first six minutes.

The first four solutions were very similar to one another not only in changing their pH values but very slightly during the electrolysis but in

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(1) loc. cit.

producing neither oxidizing substances nor ethylene; only difference being in their respective reducing power against potassium permanganate.

0.1 Per cent. solution was electrolysed by a current of much smaller density than that used in other solutions, that is, 3.6 A/dm^2. As was observed in the case of acetate(1) a current of greater density makes Kolbe's Reaction more difficult to occur in a very dilute solution. It was presumed by analogy that 0.1% solution of potassium propionate would never produce ethylene, if a current of greater density, such as 10 A/dm^2., were applied.

1.0 Per cent. solution differed from others in a remarkable manner in changing its pH value in a far broader range, and in producing some oxidizing substance, perhaps other than hydrogen peroxide, as well as ethylene.

It was thus found that the formation of ethylene by electrolysis of potassium propionate is always accompanied by that of some oxidizing substances, in exact analogy to the facts observed in the case of acetate-electrolysis. It was also discovered that the least necessary concentration of potassium propionate solution capable of undergoing Kolbe's Reaction lies somewhere between 0.7 and 1.0%, when worked under above mentioned conditions.

Table 2.

Electrolyses of dilute potassium propionate solutions, which contained 1 gr. ammonium carbonate per 100 c.c.

$D_A = 15$ A/dm^2., Temp. $= 8-10$°C.

Electrolyte % KPr	pH		Duration of Electrolysis	Exam. of the solution			C_2H_4
	orig.	after		H_2O_2	$\frac{n}{100}$ $KMnO_4$	KI+Starch	
0.1	8.5	8.8	5 min.	abs.	4 drops	$\frac{n}{100}$ $Na_2S_2O_3$ 3 drops	0.4%
0.3	,,	8.7	10	pres.	18	6	,,
0.5	,,	,,	15	,,	36	20	0.6
1.0	,,	,,	30	,,	10.7 c.c.	42	1.2

For analysis, 60 c.c. of the evolved gas were collected, and it took 5 minutes in the case of 0.1% solution, and 3½–4 minutes after the start of electrolysis in every one of the other cases.

The ethylene production even from such very dilute solutions as shown above was possibly due to the addition of ammonium carbonate which caused

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(1) loc. cit.

sufficient lowering of the anodic potential, raising the pH value of the solution, even under a comparatively higher current density such as $D_A = 15$ A/dm^2.

0.1 Per cent. solution formed hydrogen peroxide no more, this probably on account of its extreme smallness of concentration. While even the first solution in the above table produced ethylene, 1.0% solution produced it in a much less amount when compared with that evolved from the solution of the same concentration to which no ammonium carbonate was added (compare Tables 1 and 2). This is because the lowering of the anodic potential caused by the presence of ammonium carbonate reached such an extent that the solution became unsuitable for ethylene formation. In this case again, the ethylene formation was found always accompanied by the oxidizing action of the electrolysed solution.

The results of the electrolysis of a solution containing 5.0 gr. potassium propionate and 2.0 gr. propionic acid per 100 c.c. were as follows :

Table 3.

Electrolyte, (5.0 gr. potassium propionate + 2.0 gr. propionic acid per 100 c.c.) solution,

$D_A = 15$ A/dm^2., Temp. $= 8-10$°C., Original pH $= 5.0$.

Duration of Electrolysis	Exam. of the solution				C_2H_4
	pH	H_2O_2	$KMnO_4$	KI + Starch	
15 min.	5.1	trace	n/100 2.8 c.c.	n/100 $Na_2S_2O_3$ 4 drops	26.6%
30	5.3	,,	3.8	11	26.2
45	5.9	pres.	6.0	26	,,
1 hours	7.9	,,	10.0	5.0 c.c.	27.5
2	8.5	,,	51.5	6.5	14.4
3	9.2	,,	67.5	11.0	6·2
4	9.3	,,	,,	17·0	3·4
5	,,	,,	70.0	25.5	1.7
6	9.2	,,	85.0	27.6	0.6
7	,,	,,	50.0	21.5	0.2
9	9.1	,,	32.5	14.5	

The curves in Fig. 1 represent the pH, the thiosulphate and the ethylene values given in Table 3. The values on the ethylene curve corresponding to the durations 0, 1 and 1/6, 1½, 2½ and 3½ hours are not given in the table.

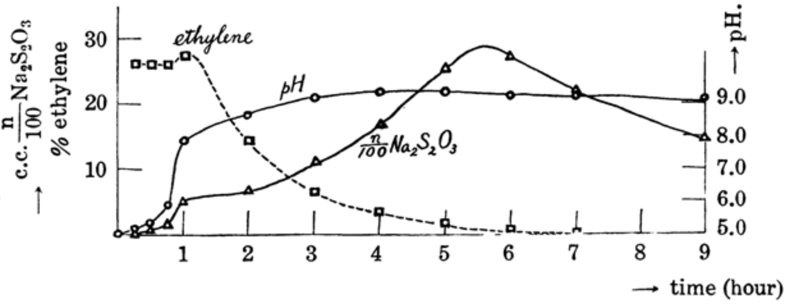

Fig. 1. Electrolyte, (5 gr. KPr + 2 gr. HPr) per 100 c.c.
$D_A = 15$ A/dm²., Temp. = 8–10°C.

The ethylene formation was almost constant for the first one hour, when the pH value quickly increased from 5.0 to nearly 8.0. It can be gathered from these facts that during the first hour the concentration of the propionate was always kept constant at the original value at the cost of that of the free acid. After that, the ethylene formation began to decrease, reaching almost nought in six hours, and the pH value, after rising gradually, remained almost constant at 9.3 during the last six hours of the experiment.

The thiosulphate consumption was slight for the first half an hour, the pH value of the solution remaining lower than 5.5; then it promptly and perceptively increased with the rise of the pH value; and at the same time the formation of ethylene was most abundant during this period. After this it increased gradually till at last it reached the maximum value before the ethylene formation finished.

In the case of potassium acetate the relation was entirely different. The thiosulphate consumption was always found greatly depressed by the intense ethane formation, and its maximum value was reached after the ethane formation had ceased.

In this case the presence of hydrogen peroxide was traced after 15 minutes' electrolysis, when the pH value was as low as 5.1. Its actual presence, however, became quite distinct 30 minutes later, when the pH value was 5.9. This also was entirely different in the case of above mentioned acetate solution, in which hydrogen peroxide was not detected even after 45 minutes' electrolysis, when the pH value was found to be 5.9.

The potassium permanganate consumption quickly increased throughout the second and third hours of the electrolysis. This fact indicates the gradual increase of the formation of reducing substances, chiefly caused by the rise of the pH value from 8.0 to 9.2.

The content of butane in the gas samples ranged from 0.2 to 0.6 volume % ; the presence of ester in the electrolysed solution could distinctly be detected by its sweet smell. But these two substances can not be considered to play an important rôle in this electrolysis.

If the formation of ethylene is assumed to be due to the decomposition of propionic peracid according to the following equation :

$$C_2H_5COOOH = C_2H_4 + H_2O + CO_2 \ldots\ldots\ldots\ldots \quad (3),$$

the decomposition reactions must be regarded to proceed in two ways, one, according to the equation (3), and the other, according to the equation (2), and these two reactions to take place side by side, to a certain extent, at the pH value ranging 8.0–9.3, and the former decomposition steadily to decline with the progress of electrolysis in contrast to the predominance of the latter.

The results of the electrolysis of a solution containing 5.0 gr. potassium propionate and 5.0 gr. ammonium carbonate per 100 c.c. are given in the following table and figure :

Table 4.

Electrolyte, (5.0 gr. potassium propionate+5.0 gr. ammonium carbonate per 100 c.c.) solution,

$D_A = 15$ A/dm^2., Temp. $= 6-7$°C., Original pH $= 8.7$.

Duration of Electrolysis	Exam. of the solution				C_2H_4	O_2
	pH	H_2O_2	$\frac{n}{100}$ $KMnO_4$	KI+Starch		
0 hour					14.8%	8.6%
1					14.2	
2	9.0	pres.	35.0 c.c.	$\frac{n}{100}$ $Na_2S_2O_3$ 2.7 c.c.	10.2	6.2
3					4.6	
4	8.6	pres.	41.0	7.5	3.2	8.0
6	8.5	,,	45.0	8.5	0.8	
8	8.0	,,	17.0	7.1	0.4	13.8

As no small amounts of oxygen were observed to be evolved, the internal oxidation in this solution must be taken as rather insignificant (compare with the corresponding case of the acetate, Table 7 in the previous paper, loc. cit.). The comparatively smaller values of potassium permanganate consumption conforms to this conjecture.

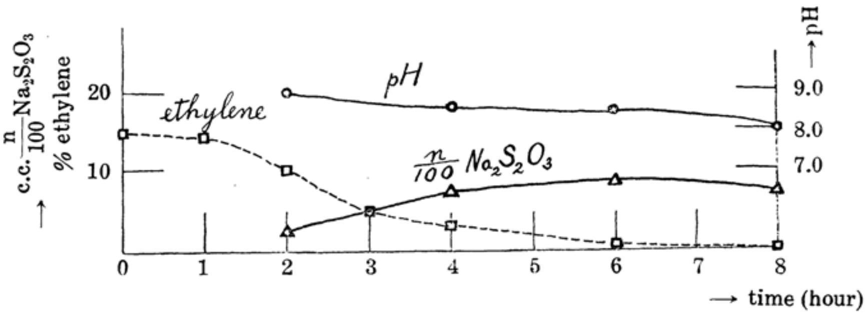

Fig. 2. Electrolyte, (5 gr. KPr + 5 gr. amm. carbonate) per 100 c.c. $D_A = 15$ A/dm²., Temp. = 7°C.

The higher value of pH, and, consequently, a lower anodic potential, caused by the addition of ammonium carbonate acted unfavourably to the discharge of propionyl ion, $C_2H_5COO^-$, as indicated by the above fact, as well as by the fact that the maximum values showing the ethylene formation and thiosulphate consumption were both remarkably lower than those given in Table 3.

Hydrogen peroxide may be regarded in the present case to have been formed soon after the start of electrolysis for the reason of the higher value of pH. The coincidence between the declination of the ethylene formation and the ascendency of the thiosulphate consumption was very clearly observed : a fact which, the author is confident, amply justifies this Peroxide Theory.

In closing this seventh paper on these researches, let the author express once more his most profound thankfulness for the constant encouragement and ever helpful suggestions, which he has received throughout his somewhat prolonged studies from his old master, Professor Dr. M. Matsui of Kyoto Imperial University.

Summary.

(1) 0.1–0.7 Per cent. solution of potassium propionate gave neither ethylene nor signs that the solution had undergone any oxidation, when electrolysed by passing a current of $D_A = 10$ A/dm². at 9–12°C.

(2) When 1.0% potassium propionate solution was electrolysed under the same conditions, ethylene was produced, and at the same time oxidizing action of the solution became observable. Hydrogen peroxide was also found present.

(3) The presence of ammonium carbonate proved so effective as to produce ethylene even from the most dilute solution. Ethylene formation was always accompanied by oxidizing action of solutions in all cases alike.

(4) Electrolyses of a solution containing 5.0 gr. potassium propionate and 2.0 gr. propionic acid and the one containing 5.0 gr. potassium propionate and as much ammonium carbonate, each in 100 c.c., were investigated.

(5) The assumption of propionyl peroxide at the intermediate product provides a very satisfactory explanation of Kolbe's Reaction and also of other reaction related to it in the electrolysis of a propionate; the production of ethylene, hydrogen peroxide and similar oxidizing substances may all be explained to take place according to the following scheme:

$$(C_2H_5COO)_2 + H_2O = C_2H_5COOH + C_2H_5COOOH,$$

$$C_2H_5COOOH = CO_2 + H_2O + C_2H_4 \text{ (Ethylene formation)},$$

$$C_2H_5COOOH + H_2O = C_2H_5COOH + H_2O_2 \text{ (Hydrogen peroxide formation)}.$$

(6) The difference observed between electrolyses of potassium propionate and potassium acetate will easily be understood, if we take notice of the higher stability of propionyl peroxide in comparison with acetyl peroxide.

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