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

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Various theories have been advanced to explain the mechanism of Kolbe's reaction, since the great Leipzigian professor discovered it in 1849. None of these theories, however, is convincing for lack of sufficient evidence. The present author has been studying the electrolyses of ammonium and potassium acetates in aqueous solution for some time. The results of his investigation have been published in the Journals of the Chemical Society of Japan in the vernacular language (**51** (1930), 126; **51** (1930), 632; **52** (1931), 249; **52** (1931), 756).

During the author's examination of acetate solutions of smaller concentration, his notice was drawn to the fact that the colours of the indicator added to the electrolyte for pH determination had entirely disappeared in course of the experiments. This quite unanticipated phenomenon prompted him to take in hand a fresh investigation on the machanism of the so-called Kolbe's reaction.

The electrolytes after having been electrolysed for some time were proved to contain certain oxidizing substances, setting iodine free from potassium iodide solution. It is now the author's purpose to determine the amounts of such oxidizing substances formed in course of the electrolyses of the two acetates, and compare them with those of ethane, which is formed simultaneously.

Experimental.

The apparatus used for electrolysis were the same as those mentioned in the preceding papers, while the conditions under which the electrolyses were carried out, throughout the present investigation, were as follows:

Current density: 10 A/dm^2 excepting the two cases of 0.1% NH_4Ac and 0.1% KAc, where 9 A/dm^2 and 5.1 A/dm^2 were applied respectively.

Temperature: 8–10° C., excepting the cases of electrolytes of the smallest concentrations, where the temp. was raised to 15–20° C.

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 was acidified with an excess of sulphuric acid, and titrated by means of n/100 $KMnO_4$ solution.

Potassium iodide and starch test: 20 c.c. of the sample solution was added to KI solution, and iodine set free was titrated with n/100 thiosulphate solution, using a starch solution as the indicator. When reaction is thought to have ceased, a little more KI was added to ascertain its sufficiency.

Table 1.

Electrolyte		Duration of electrolysis	After electrolysis				C_2H_6% in the gas sample
composition	pH		pH	H_2O_2	$KMnO_4$	KI+starch	
NH_4Ac 0.1%	6.65	2½ min.	6.6	abs.	1 drop	no colouration	0
,, 0.3	6.78	6	6.8	trace	1	trace	0
,, 0.5	6.8	10	6.9	,,	3	Thiosulphate 1 drop*	0.1
,, 0.7	,,	14	7.8	pres.	25	11	13.7
,, 1.0	6.9	2	7.5	abs.	3	1	—
,, ,,	,,	20	8.2	pres.	37	1	28.0
,, 3.0	7.0	30	8.3	,,	61	4	28.8
,, ,,	,,	60	,,	,,	255	2	—
,, 5.0	7.05	½	7.1	abs.	2	1	29·3
,, ,,	,,	48	8.2	pres.	130	8	—
,, ,,	,,	96	8.3	,,	750	32	—

* 25 drops = 1 c.c.

From the above table we may gather interesting relations existing between ethane formation and oxidizing action of the electrolysed solutions on potassium iodide. The first two solutions in Table 1 neither evolved ethane, nor gave oxidizing substances (the details of the electrolytic gases were given in the latest paper, loc. cit.). By the 0.5% NH_4Ac solution, which comes third in the table, however, ethane was evolved for the first time, and at the same time some oxidizing substances were found to exist in the solution; like results were obtained in the rest of solutions.

With regard to the 5.0% NH_4Ac solution, the last mentioned in the table, the amount of oxidizing substances was observed gradually to increase as electrolysis went on, while, on the contrary, the quantity of ethane to become less and less. The latter fact was already referred to in the previous paper.

Again, hydrogen peroxide became detectable when electrolysis was continued for some time (in last two cases) but not immediately after its inception (as in the first case). These facts will be more fully stated in the subsequent case of potassium acetate solutions.

The consumption of $KMnO_4$ solution suggests the presence of certain reducing substances. They may be hydrogen peroxide, some other peroxide-like substances, formaldehyde, or the like. The amount of such reducing substances was also observed to increase with the progress of electrolysis.

The following table shows the results obtained of electrolyses of potassium acetate solutions (0.1%—5.0%).

Table 2

Electrolyte		Duration of electrolysis	After electrolysis				C_2H_6% in the gas sample
composition	pH		pH	H_2O_2	$KMnO_4$	KI+starch	
KAc 0.1%	5.85	2 min.	5.9	abs.	0 drop	No colouration	0
,, 0.4	5.9	6.4	,,	,,	,,	,,	0.2
,, 0.5	,,	8	,,	,,	4	trace	2.8
,, 1.0	,,	15	8.2	pres.	28	Thiosulphate 7 drops	15.2
,, 5.0	6.0	1h. 15m.	8.5	,,	15.5 c.c.	,, 70	27.8

The percentages of ethane evolved from 1.0 and 5.0% potassium acetate solutions were determined by analysing gas samples collected during the first 4 and 3 minutes of electrolysis respectively. In these cases of potassium acetate, the formation of ethane was observed to take place always accompanied with that of oxidizing substances, just as much as in the case of the ammonium salt.

It is also noticeable that when the concentration of the electrolyte was comparatively small, or the pH value of the solution was but slightly raised above 6 no trace of hydrogen peroxide, which seems to have an important bearing on the oxidizing substances in question, was detected. It will, therefore, be highly interesting to push on investigation along this line.

To know how the solutions of potassium acetate behave in course of electrolysis on a broader range of pH, the solutions acidified with acetic acid, or made alkaline by the addition of ammonium carbonate were investigated. The following tables and figures show the results of the electrolysis of a solution, which contained 5.0 gr. KAc and 1.4 gr. HAc per 100 c.c. Although the electrolytic gas in this case was not analyzed, it was approximately estimated by adopting the principle that the electrolytes of similar compositions give similar ethane formation curves, and that the duration of ethane formation is in proportion to the concentration of a like electrolyte, if the current of the same anodic density be applied, the said principle being derived from the results of the experiment No. 4, which treated the (20% KAc+5% HAc) solution, as was described in the first paper and the experiments Nos. 1, 5, 8, 11, 14, 17, etc. (vid. also the third paper (loc. cit.)) Thus it may be regarded that ethane formation in the above case will reach the maximum point three quarters of an hour after the start of an electrolytic process, and is about through in another 45 minutes. These relations lead to the conclusion that ethane formation predominates over the formation of oxidizing substances at the earlier stages of electrolysis, but vice versa at the later stages.

Table 3.

Electrolyte, (KAc 5.0 gr. + HAc 1.4 gr.) per 100 c.c.,
Original pH = 5.0, D_A = 10 A/dm^2, Temp. = 8—10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
35 min.	5.5	abs.	4 drops	Thiosulphate 4 drops
45	5.9	,,	,,	5
50	7.3	pres.	20	16
60	7.5	,,	,,	19
70	8.5	,,	2.3 c.c.	17
1½ hours	8.75	,,	6.5	3
2	,,	,,	22	68
2½	8.7	,,	53	9.8 c.c.
3¼	,,	,,	110	14.6
4	,,	,,	120	16.4
5	—	,,	160	14.6

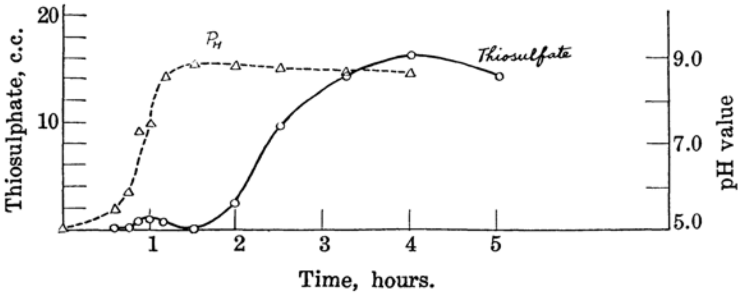

Fig. 1.

(KAc 5.0 gr. HAc 1.4 gr. per 100 c.c.) solution, D_A=10 A/dm^2, Temp.=8−10°C.

If we assume that acetyl peroxide is first formed at the anode, and the most of it is decomposed at the earlier stages of electrolysis according to the following equation:

$$\underset{\text{acetyl peroxide}}{(CH_3{\cdot}COO)_2} = \underset{\text{ethane}}{CH_3{\cdot}CH_3} + 2\,CO_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

and only a small portion of it remains as such, or is decomposed according to the following scheme:

$$\left.\begin{aligned} (CH_3{\cdot}COO)_2 + H_2O &= CH_3{\cdot}COOH + \underset{\text{acetic peracid}}{CH_3{\cdot}COOOH}, \\ CH_3{\cdot}COOOH + H_2O &= CH_3{\cdot}COOH + \underset{\text{hydrogen peroxide}}{H_2O_2} \end{aligned}\right\} \ldots\ldots\ldots \quad (2),$$

the decomposition of acetyl peroxide according to the equation (1) must be regarded to decline at the later stages of electrolysis, the chemical change (2) predominating over it. It will be superfluous to say that the two acids involved in the equation (2) take the form of the corresponding salts, when the solution becomes alkaline. This assumption will go a long way to explain the fact, observed so far.

As hydrogen peroxide, which is one of the final decomposition products of acetyl peroxide, easily decomposes in alkaline solutions, its total amount can not continue to increase with the progress of electrolysis, which naturally involves the alkalinity of the solution, but must begin to decrease at a certain point. This explanation will satisfactorily account for why the thiosulphate curve in Fig. 1 falls after once passing over the maximum point. Hydrogen peroxide could not be detected until the electrolysis has been continued for three quarters of an hour, during which the pH of the solution was still below 6.0. Then the pH rose quickly and reached above 7.0 some five minutes later; thereafter hydrogen peroxide was found always present.

The reaction expressed by the second equation of the chemical change (2) is reversible as was pointed out by W.H. Hatcher and G.W. Holden.⁽¹⁾ If so, it is easily conceivable that the formation of hydrogen peroxide according to the second equation is governed by the condition of the electrolyte, in such a manner that an alkaline or a dilute solution favours the formation of hydrogen peroxide, while an acidic or a concentrated one acts contrarily.

The reason, why hydrogen peroxide became detectable after having been absent for the first 45 minutes of electrolysis, can be easily understood, if we take into consideration the pH value of the solution on the one hand

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(1) *Trans. Roy. Soc. Canada* [3] **21**, Sect. III. (1927), 237–243: C. 1928, I, 1929.

and the concentration of it on the other. The following table and Fig. 2 relate to the solution of KAc 10.0 gr. and HAc 2.8 gr. per 100 c.c.

Table 4.

Electrolyte, (KAc 10.0 gr. + HAc 2.8 gr.) per 100 c.c.,
Original pH=5.0, D_A=10 A/dm², Temp.=8–10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
½ hour	5.1	abs.	5 drops	Thiosulphate 2 drops
1½	6.9	,,	10	7
1⅔	7.4	pres.	17	14
2	8.7	,,	2 c.c.	8
3	,,	,,	10	26
4	,,	,,	40	8.6 c.c.
5	,,	,,	110	21.6
6	8.65	,,	105	25.9
8	8.55	,,	150	18.6

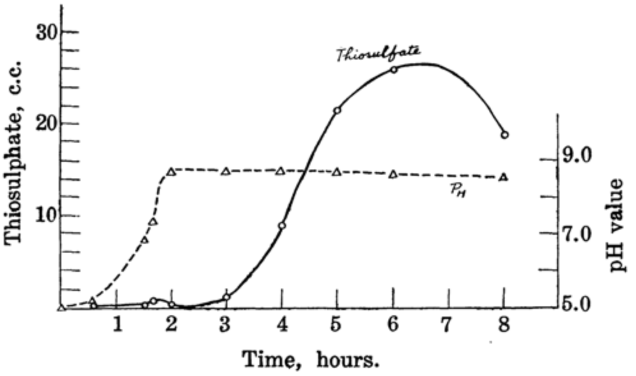

Fig. 2.

$\left(\begin{matrix}\text{KAc 10.0 gr.}\\ \text{HAc 2.8 gr.}\end{matrix}\text{ per 100 c.c.}\right)$ solution, D_A=10 A/dm², Temp.=8—10°C.

By the same reason as with the previous case it can be assumed that the ethane evolution from the present solution reaches the maximum point somewhere between 1½–2 hours after the commencement of electrolysis; after that it gradually falls until it is nearly done with about an hour later.

Let us now proceed to examine the thiosulphate curve of Fig. 2. After passing a maximum point the curve falls to a minimum point two hours after the start; and then it suddenly leaps up to another maximum point again. The maximum value of thiosulphate consumption is 26.5 c.c. in this case, whereas it was 16.5 c.c. in the preceding one.

It will be readily seen that the maximum point of the ethane formation curve thus coincides with the minimum point of the thiosulphate consumption curve, and the lowest part of the former corresponds with the highest part of the latter. Besides, the maximum value of thiosulphate consumption of the second KAc solution is much higher than that of the first one, although not so high as proportional to the concentration (loc. cit.).

These facts will demonstrate, the author is confident, that ethane has its origin in acetyl peroxide.

Table 5 and Fig. 3 shown below illustrate the results of the electrolysis of the solution containing KAc 20 gr. and HAc 5.6 gr. in 100 c.c. The ethane curve in this figure does not represent this solution but that containing 20% KAc and 5% HAc instead (the first paper, loc. cit.). But the difference between these two solutions being very slight, the curve may be taken as that of the former without significant error.

Table 5.

Electrolyte, (KAc 20.0 gr. + HAc 5.6 gr.) per 100 c.c.,
Original pH = 5.1, $D_A = 10$ A/dm², Temp. = 8—10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
¼ hour	5.15	abs.	5 drops	Thiosulphate 1 drop
2½	5.7	,,	—	3
3	7.5	,,	12	9
4	8.7	pres.	2.0 c.c.	5
5	,,	,,	5.5	9
8	8.8	,,	120	12.5 c.c.
10	8.7	,,	145	14.7
13	8.5	,,	220	31.5
16	—	,,	270	18.9

Coincidences between several corresponding points on the ethane and thiosulphate curves can clearly be noticed here. The maximum value of thiosulphate consumption is 31.5 c.c., being greater than those of the foregoing two solutions. The hours needed for the attainment of these maximum points were nearly proportional to the concentration of the electrolytes; being 4, 6.5 and 13 hours respectively in these three cases.

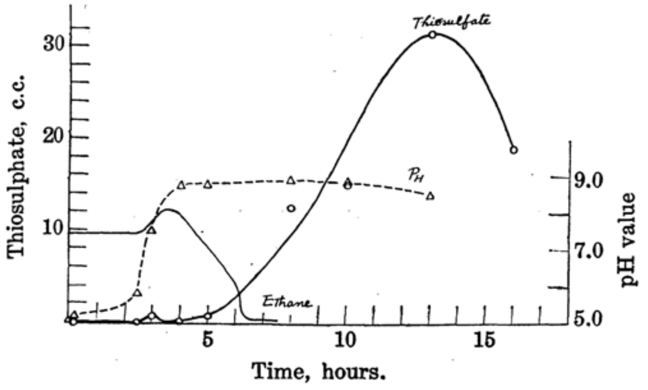

Fig. 3.

$\left(\begin{array}{l}\text{K Ac 20.0 gr.}\\ \text{H Ac 5.6 gr.}\end{array}\text{per 100 c.c.}\right)$ solution, $D_A=10$ A/dm^2, Temp.=8—10°C.

This fact upholds once more, it seems, that acetyl peroxide is one of the principal products of the electrolysis of potassium acetate solutions.

Table 6.

Electrolyte, (KAc 40.0 gr. + HAc 12.0 gr.) per 100 c.c.,
Original pH = 5.1, $D_A = 10$ A/dm^2, Temp. = 8—10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
$\frac{1}{2}$ hour	5.15	abs.	16 drops	Thiosulphate 4 drops
$5\frac{1}{2}$	6.0	,,	37	10
$6\frac{1}{2}$	7.3	,,	35	17
8	9.0	,,	32	9
$9\frac{3}{4}$	9.3	,,	15	20

The electrolysis of the (KAc 40 gr. + HAc 12 gr.) per 100 c.c. solution has been traced only so far as 9 hours after the start. The minimum point of thiosulphate consumption lies, at least in this limited range of electrolysis, perhaps at a period of about 8 hours after the start, a fact which can be readily estimated from the foregoing data.

No hydrogen peroxide was detected in this case, even after nearly 10 hours' operation, when the pH value was already as high as 9.3. In the case of the (KAc 20 gr. + HAc 5.6 gr.) per 100 c.c. solution hydrogen peroxide was detected at pH = 8.2, but not at pH = 7.5 yet. In the case of the (KAc 10 gr. + HAc 2.8 gr.) per 100 c.c. solution hydrogen peroxide was detected at pH = 7.4, but not at pH = 6.9 yet. In the case of the (KAc 5.0 gr. + HAc 1.4 gr.) per 100 c.c. solution, it was detected at pH = 7.3, but not at pH = 5.9 yet.

Hydrogen peroxide, which is one of the most interesting compounds, not only from the scientific, but technical, view, is considered so far not to be produced by the anodic reaction directly.

If we assume that hydrogen peroxide makes its appearance according to the equations (2) we can easily understand, by admitting the explanation given above, the relation between its formation and pH value in each of these solutions, and also the fact that the more concentrated are the solutions, the less capable are they of forming H_2O_2 in spite of a comparatively higher value of pH.

The author made an observation in the first paper that a potassium acetate solution containing ammonium carbonate behaves quite differently from other cases under electrolysis, with extraordinarily small but constant yields of ethane and oxygen throughout the process; the second paper was concerned to somewhat detailed examinations of a similar nature. The following table deals with electrolysis of (KAc 10 gr. + Amm. carbonate 5 gr.) per 100 c.c. solution.

Table 7.

Electrolyte, (KAc 10.0 gr. + Amm. carbonate 5.0 gr.) per 100 c.c., Original pH = 8.6, D_A = 10 A/dm^2, Temp. = 8–10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
0 hour	8.6	—	—	Thiosulphate 0 drop
1	,,	pres.	35 c.c.	10
2½	,,	,,	70	1.3 c.c.
5	8.5	,,	250	3.3
7	,,	,,	125	7.5
9	8.1	,,	160	10.4

The comparatively higher value of the original pH of this solution makes us understand that hydrogen peroxide is formed shortly after the start of electrolysis.

Extraordinarily efficient internal oxidation of this solution (vid. the first paper), by corresponding with the very small yields of ethane and oxygen, signifies that a large amount of methyl alcohol is formed there. The more of the $CH_3 \cdot COO$ group of the acetate is changed into the form of methyl alcohol, the less will take the form of ethane or acetyl peroxide, the latter of which may be further transformed into hydrogen peroxide. The comparatively smaller amounts of ethane (vid. the second paper) and thiosulphate consumption in Table 7 both conform to this expectation.

In conclusion of this paper the author begs to express his deepest sense of indebtedness to Professor Dr. M. Matsui of Kyoto Imperial University for his unfailing encouragement and suggestions for the continuation of these studies.

Summary.

(1) The relation between ethane and oxidizing substances in the solutions formed by the electrolyses of acetate solutions is discussed.

(2) It is demonstrated that acetyl peroxide is first formed at the anode, and that ethane is one of its decomposition products.

(3) The presence of hydrogen peroxide in the solutions after electrolysis is attributed to the following hydrolyses of acetyl peroxide:

$$(CH_3 \cdot COO)_2 + H_2O = CH_3 \cdot COOH + CH_3 \cdot COOOH\,,$$
$$CH_3 \cdot COOOH + H_2O = CH_3 \cdot COOH + H_2O_2\,.$$

(4) It is discussed how the formation of hydrogen peroxide is related to the pH value of the solution on the one hand and to the concentration of the solution on the other.

(5) The relation existing between the ethane and the hydrogen peroxide formations is also discussed.

(6) It is concluded that the facts observed in the experiments so far carried out by the writer can well be explained by assuming the intermediate formation of acetyl peroxide.

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