The Relation between Kolbe's Reaction and Hydrogen Ion Concentration. VIII.

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Anodic oxidation of acetate and propionate was studied in the foregoing parts(1) of this paper, and, later on, electrolytic formation of persulphate was investigated by one of the present writers (R.M.) and his collaborators(2). The present paper describes a study of preceding two electrolyses combined together, i.e., anodic reactions which take place by electrolysing a mixture of acetate and sulphate. Anolytes which contained sulphuric acid, ammonium sulphate, acetic acid, and ammonium acetate in various proportions were electrolysed with sulphuric acid as the catholyte and the anodic gases and peroxidic substances produced in the anolytes were investigated. The results of the gas analyses lead to an assumption that there is contained in it a new gaseous substance which was not known hitherto with a chemical formula $(CO_2)_2$, and which seems to have an important bearing on the peroxide theory.

Experimental. The interior of a porcelain cylinder makes the anode chamber, which is equipped with a rubber stopper to which a platinum-wire anode, a thermometer, a stirrer and two bent tubes are inserted. The platinum anode is 0.5 mm. thick and 20.7 cm. long with a total effective surface of 3.25 cm^2., which makes a spiral surrounding the thermometer (Fig. 1).

The cathode also consists of a platinum-wire which is as thick as the anode and 45 cm. long. The electrolytic cell, which is a glass beaker, is surrounded with ice water to keep the temperature of the anolyte at 10°C. Current is so regulated as to supply a nearly definite amount of electricity which is measured by means of a copper coulometer. Anodic current density, D_A, is varied

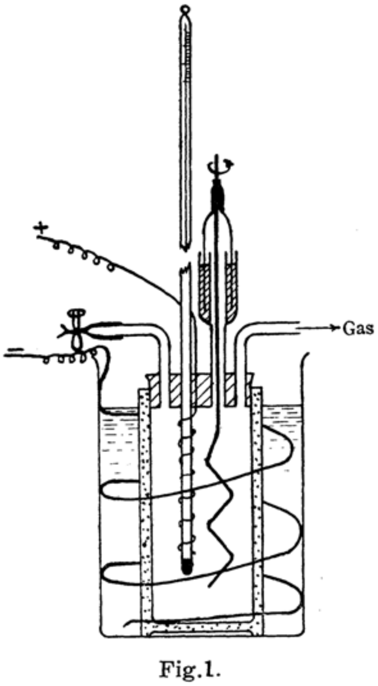

Fig.1.

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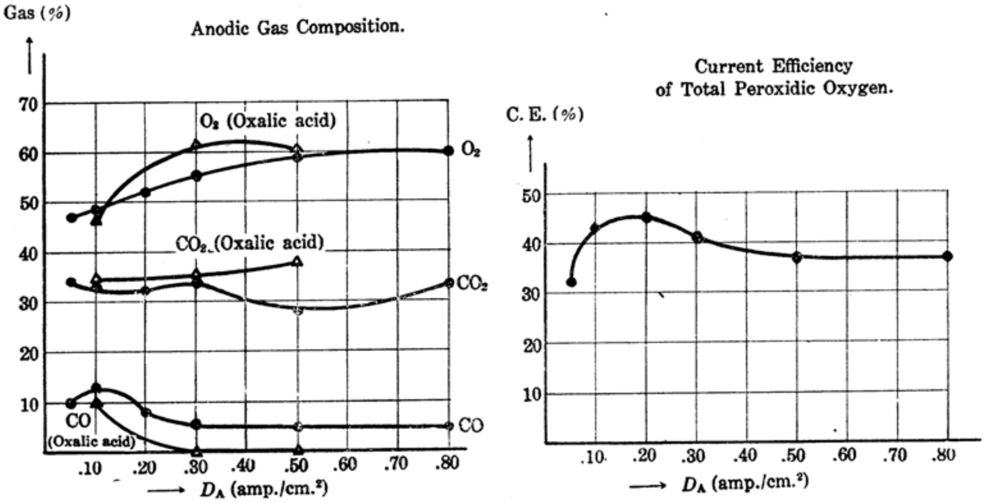
(1) R. Matsuda and his collaborators, *J. Chem. Soc., Japan*, **51** (1930), 126; *ibid.*, **51** (1930), 632; *ibid.*, **52** (1931), 249: 756; this Bulletin, **7** (1932), 18, 297; *Compl. Abstr. J. Chem. Lit.*, Ser. 2, **6** (1932), 85 B.

(2) R. Matsuda and his collaborators, this Bulletin, **11** (1936), 1, 650; *ibid.*, **12** (1937), 331, 425; *ibid.*, **14** (1939), 72.

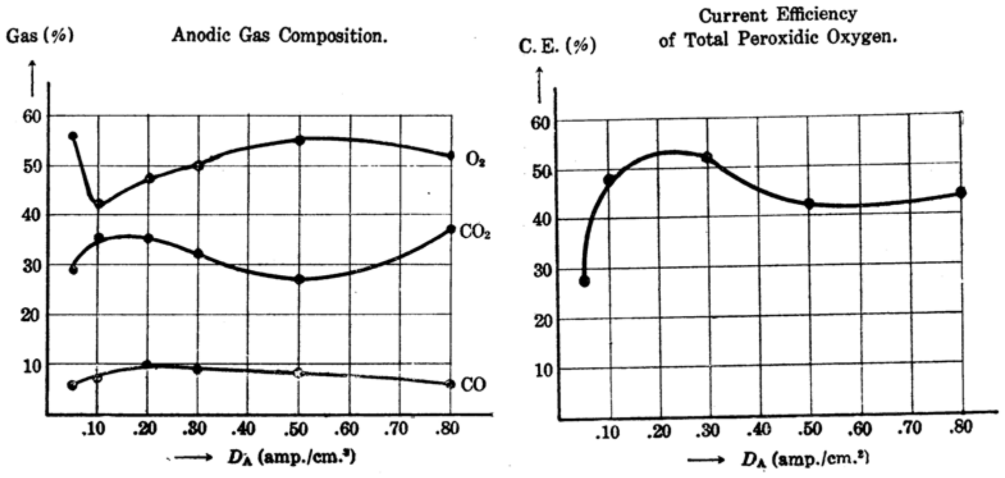
from 0.05 to 0.80 amp./cm². The porcelain cylinder is filled with an anolyte which measures 65 c.c., the two bent tubes being filled, as well, with the same solution at the beginning of the electrolysis. The catholyte consists of 90 c.c. 6 N sulphuric acid, unless otherwise mentioned.

The electrolysed anolyte is first tested qualitatively for hydrogen peroxide by titanium sulphate and then Caro's acid, persulphuric acid and



Anolyte $\begin{pmatrix} 10\,\text{N}\ H_2SO_4 \\ 2\,\text{N}\ CH_3COOH \end{pmatrix}$ Catholyte $6\,\text{N}\ H_2SO_4$

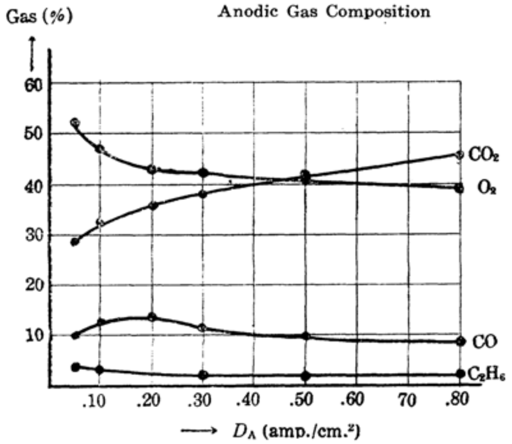
Fig. 2.



Anolyte $\begin{pmatrix} 8\,\text{N}\ H_2SO_4 \\ 2\,\text{N}\ (NH_4)_2SO_4 \\ 2\,\text{N}\ CH_3COOH \end{pmatrix}$ Catholyte $6\,\text{N}\ H_2SO_4$

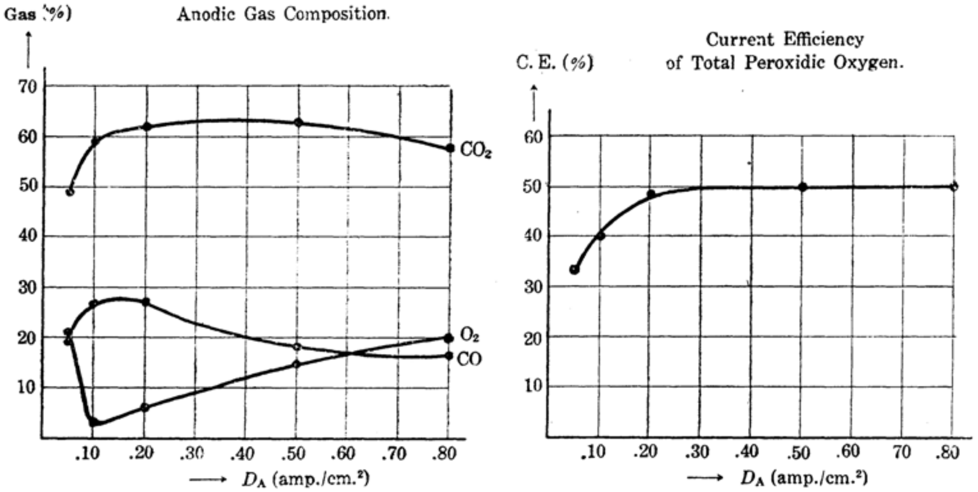
Fig. 3.

hydrogen peroxide are titrated after K. Glen's method⁽³⁾, but the pH of the anolyte is not determined. The anodic gas collected over a solution which is saturated with sodium chloride as well as with coal gas, is analysed according to Hempel's method. The oxygen used for explosion analysis is proved to be pure, containing neither nitrogen nor carbon dioxide.



Anolyte $\begin{pmatrix}5\text{ N } H_2SO_4\\ 2\text{ N } CH_3COONH_4\end{pmatrix}$ Catholyte 6 N H_2SO_4

Fig. 4.



Anolyte $\begin{pmatrix}5\text{ N } (NH_4)_2SO_4\\ 2\text{ N } CH_3COOH\end{pmatrix}$ Catholyte 6 N H_2SO_4

Fig. 5.

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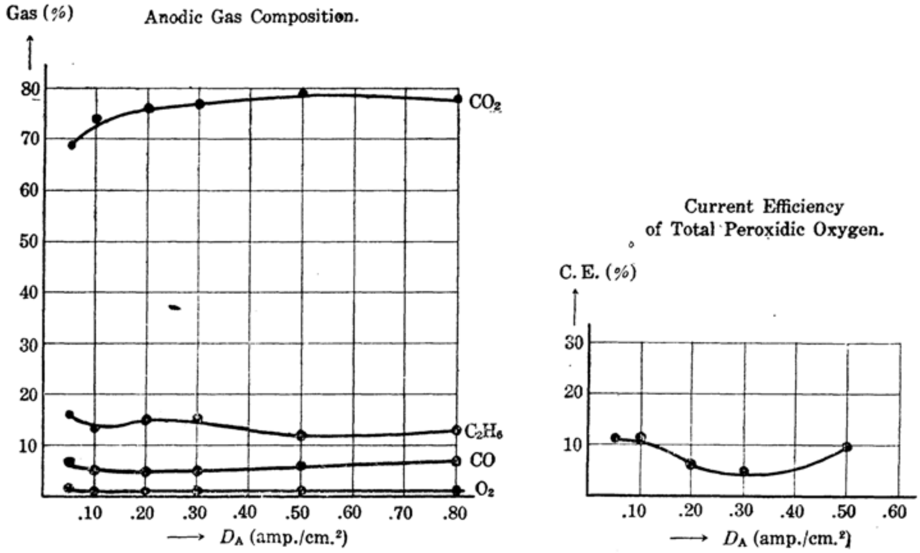
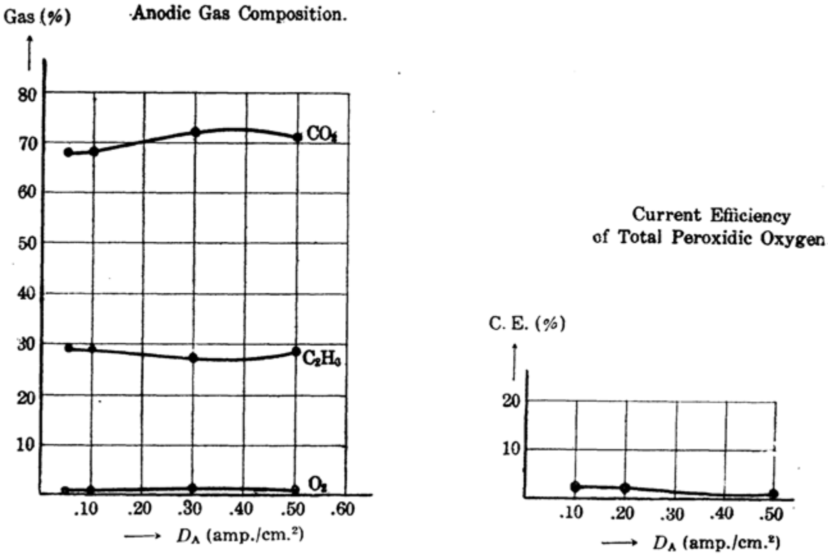
(3) *Z. anorg. u. allg. Chem.*, **195** (1931), 61.



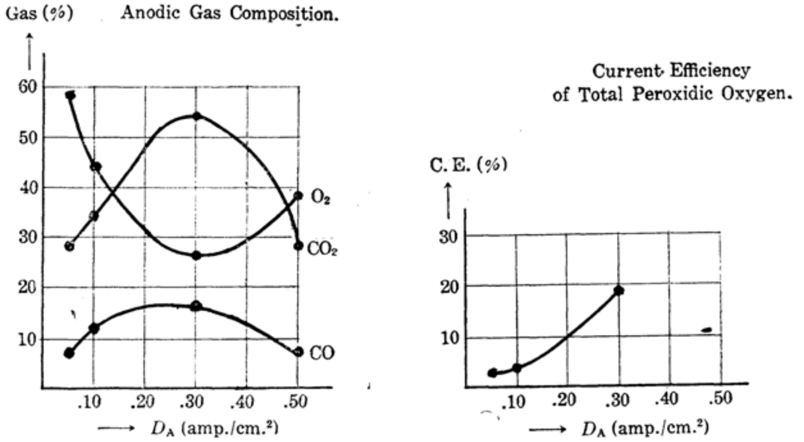
Anolyte $\begin{pmatrix} 5\,\text{N}\ (NH_4)_2SO_4 \\ 1\,\text{N}\ CH_3COONH_4 \\ 1\,\text{N}\ CH_3COOH \end{pmatrix}$ Catholyte 6 N H_2SO_4

Fig. 6.



Anolyte $\begin{pmatrix} 5\,\text{N}\ (NH_4)_2SO_4 \\ 2\,\text{N}\ CH_3COONH_4 \end{pmatrix}$ Catholyte 6 N H_2SO_4

Fig. 7.



Anolyte $\begin{pmatrix}0.44\,\text{N}\ \text{CuSO}_4 \\ 2\,\text{N}\ \text{CH}_3\text{COOH}\end{pmatrix}$ Catholyte 6 N H_2SO_4

Fig. 8.

Following generalisations can be drawn from the data in Table 1. Carbon dioxide is produced from all the anolytes, No. 1 to No. 7, that is to say, complete oxidation takes place in each anolyte. And the lower the acidity of the anolyte, the more carbon dioxide is produced. Heavy hydrocarbon is not produced from any of the anolytes mentioned above. But when a solution which contains only acetate is electrolysed, Kolbe's reaction takes place and the anodic gases are shown to contain a little heavy hydrocarbon beside ethane. Oxygen is always evolved from the anolytes, but its proportion is small in some cases, e.g., 1 to 2%, and less than 1% in the anolytes No. 5 and No. 6 respectively. And the higher the acidity of the anolyte, the more oxygen is evolved. Carbon monoxide which is a product of incomplete oxidation is evolved in all cases but the anolyte No. 6. When the three anolytes, No. 4, 5, and 6 which contain no free sulphuric acid are compared, the proportion of carbon monoxide increases with the acidity of the anolyte.

Ethane is not produced from free acetic acid, but it is formed, if the anolyte contains ammonium acetate, even in the presence of free sulphuric acid. $(CO_2)_2$, which is a hypothetical substance, is produced to a small extent from the anolyte No. 3 which is acid with sulphuric acid, and to a less extent from the anolyte No. 5 which is acid with acetic acid, but none from the neutral anolyte No. 6 which nevertheless produces ethane. Nor it is formed from any anolyte which does not produce ethane.

The total volume of anodic gases increases, in general, as the acidity of the anolyte lowers. The total volume of oxygen at S. T. P. evolved from an anolyte which contains free sulphuric acid per 0.67 amp.-hour is remarkably large, and though it is comparatively small from an anolyte which contains no free sulphuric acid, it increases with the acidity of the anolyte.

Table 1.

Anolyte	Anodic Gases									
	Approximation on an average in %								Total Gas Vol. per 0.67 amp.-h.	Total O_2 Vol. per 0.67 amp.-h.
	CO_2	C_nH_{2n}	O_2	CO	C_2H_6	$(CO_2)_2$	unkn.	Total		
No. 1 $\begin{pmatrix} 10\,\text{N}\ H_2SO_4 \\ 2\,\text{N}\ CH_3COOH \end{pmatrix}$	32	0	55	6	0	0	7	100	25～50 c.c.	14～28 c.c.
No. 2 $\begin{pmatrix} 8\,\text{N}\ H_2SO_4 \\ 2\,\text{N}\ (NH_4)_2SO_4 \\ 2\,\text{N}\ CH_3COOH \end{pmatrix}$	33	0	52	7	0	0	8	100	20～45 ,,	10～23 ,,
No. 3 $\begin{pmatrix} 5\,\text{N}\ H_2SO_4 \\ 2\,\text{N}\ CH_3COONH_4 \end{pmatrix}$	40	0	42	10	3	<1	5	100	10～27 ,,	4～11 ,,
No. 4 $\begin{pmatrix} 5\,\text{N}\ (NH_4)_2SO_4 \\ 2\,\text{N}\ CH_3COOH \end{pmatrix}$	60	0	15	20	0	0	5	100	24～45 ,,	4～7 ,,
No. 5 $\begin{pmatrix} 5\,\text{N}\ (NH_4)_2SO_4 \\ 1\,\text{N}\ CH_3COONH_4 \\ 1\,\text{N}\ CH_3COOH \end{pmatrix}$	76	0	1	6	14	<1	3	100	220～240 ,,	2～3 ,,
No. 6 $\begin{pmatrix} 5\,\text{N}\ (NH_4)_2SO_4 \\ 2\,\text{N}\ CH_3COONH_4 \end{pmatrix}$	70	0	<1	0	28	0	2	100	280～440 ,,	<1 ,,
No. 7 $\begin{pmatrix} 0.44\,\text{N}\ CuSO_4 \\ 2\,\text{N}\ CH_3COOH \end{pmatrix}$	40	0	40	12	0	0	8	100	85～147 ,,	34～65 ,,

Table 2. Current Efficiency in % of Peroxidic Oxygen.

Anolyte	C_A (amp./cm.^{2})	0.05	0.10	0.20	0.30	0.50	0.80
No. 1 (10 N H_2SO_4 2 N CH_3COOH)	H_2SO_5	0.3	0.3	0.2	0.1	0.3	0.1
	H_2O_2	0.1	0.1	0.1	0.1	0.1	0.1
	$H_2S_2O_8$	31.1	42.1	44.5	41.1	37.2	36.5
	Total	31.5	42.5	44.8	41.3	37.6	36.7
No. 2 (8 N H_2SO_4 2 N $(NH_4)_2SO_4$ 2 N CH_3COOH)	H_2SO_5	0.1	0.1	0.2	0.1	0.1	0.1
	H_2O_2	0	0.1	0.1	0.1	0.1	0
	$H_2S_2O_8$	28.3	47.6	55.6	51.9	41.8	43.6
	Total	28.4	47.8	55.9	52.1	42.0	43.7
No. 4 (5 N $(NH_4)_2SO_4$ 2 N CH_3COOH)	H_2SO_5	0.1	0.1	0.1	—	0.1	0.1
	H_2O_2	0.1	0.1	trace	—	trace	0.1
	$H_2S_2O_8$	33.2	40.1	49.0	—	51.2	49.2
	Total	33.4	40.3	49.1	—	51.3	49.4
No. 5 (5 N $(NH_4)_2SO_4$ 1 N CH_3COONH_4 1 N CH_3COOH)	H_2SO_5	0.5	0.5	0.5	0.5	0.5	—
	H_2O_2	trace	trace	0	trace	trace	0
	$H_2S_2O_8$	10.4	10.4	5.4	4.5	9.1	—
	Total	10.9	10.9	5.9	5.0	9.6	—
No. 6 (5 N $(NH_4)_2SO_4$ 2 N CH_3COONH_4)	H_2SO_5	—	0.3	0.5	—	0.2	—
	H_2O_2	—	0	0	—	0	—
	$H_2S_2O_8$	—	1.3	1.6	—	1.3	—
	Total	—	1.6	2 1	—	1.5	—
No. 7 (0.44 N $CuSO_4$ 2 N CH_3COOH)	H_2SO_5	0	0.3	—	0.1	—	—
	H_2O_2	0.5	0.4	—	trace	—	—
	$H_2S_2O_8$	2.7	3.5	—	18.5	—	—
	Total	3.2	4.2	—	18.6	—	—

The current efficiencies with respect to each of the peroxidic substances are given in Table 2. As methyl orange changed yellow, the titration of the anolyte No. 3 was not possible. The maximum current efficiency of the total peroxidic oxygen is 55% (the anolyte No. 2) and the minimum is 2% (the anolyte No. 6). It is observed that the total peroxidic oxygen increases with the acidity of the anolytes, when various anolytes are compared, and also that it decreases when oxygen evolution prevails and vice versa, when it is compared over the whole range of D_A. The bulk of the peroxidic oxygen is due to persulphuric acid, and Caro's acid comes next to it, hydrogen peroxide being found very little in each case. Hydrogen peroxide is produced in traces from the anolyte

No. 5 which is weakly acid, but none from the neutral anolyte No. 6, and generally speaking, the more acid the anolyte, the more it is found.

On $(CO_2)_2$ $^{(4)}$. When a gas sample, which was assumed to contain $(CO_2)_2$, was treated with the potash pipette to estimate carbon dioxide at the beginning of gas analysis, white fume was observed to take place. When an explosion sample out of the combustible residue after removal of carbon dioxide, heavy hydrocarbon, oxygen, and carbon monoxide was mixed with an excess of oxygen and subjected to electric discharge, it was observed that white and dense fume continued to appear for some time between the electrodes, falling down on the surface of mercury in the pipette. And then explosion followed, but never before. Some sample did not explode in spite of continued discharge by which white fume was yet produced. When the gases after explosion were treated with the potash pipette, another white fume was observed to take place. The electrodes of the pipette were covered with brownish black coating.

Table 3. Results of some Explosion Analyses.

Anolyte No. 3 $\begin{pmatrix} 5\,\text{N}\ H_2SO_4 \\ 2\,\text{N}\ CH_3COONH_4 \end{pmatrix}$

$D_A = 0.80$ amp./cm^2

Sample	No. 1 (c.c.)	No. 21 (c.c.)	No. 24 (c.c.)	No. 27 (c.c.)
The volume of the sample	2.3	1.7	1.8	1.8
Contraction on explosion	1.4	1.0	1.1	1.2
CO_2 produced on explosion	1.4	1.2	1.1	1.3
The volume of residue	1.6 (1.6)	1.1 (1.1)	1.2 (1.25)	1.2 (1.15)
O_2 consumption	2.1 (2.1)	1.6 (1.6)	1.6 (1.65)	1.9 (1.86)
C_2H_6	0.6	0.46	0.47	0.53
$(CO_2)_2$	0.1	0.14	0.08	0.12

The ratios in volume of the contraction to the carbon dioxide on combustion of metane and ethane are as follows:

$$\frac{\text{contraction}}{CO_2} = 2.0 \qquad \text{for} \qquad CH_4\,,$$

$$\text{and} \qquad \frac{\text{contraction}}{CO_2} = 1.25 \qquad \text{for} \qquad C_2H_6\,.$$

The corresponding ratios obtained from figures in Table 3, however, are equal to or less than unity. It is eventually assumed that a gas with a chemical formula $(CO_2)_2$, is hypothetically present with ethane if the latter is the only hydrocarbon in the sample and also that explosion results in the two reactions as shown by the following equations:

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(4) R. Matsuda, *J. Chem. Soc., Japan*, **61** (1940), 638.

$$C_2H_6+3\frac{1}{2}\,O_2 = 2\,CO_2+3\,H_2O\ ,$$

$$(CO_2)_2 = 2\,CO_2\ :$$

one is the complete oxidation of ethane which brings about contraction, and the other is the decomposition of $(CO_2)_2$ into carbon dioxide which brings about expansion, both reactions producing carbon dioxide.

Let x = volume of ethane,
and y = volume of $(CO_2)_2$:
a = contraction on explosion,
and b = volume of carbon dioxide produced.

Then,

$$2\frac{1}{2}x-y = a\ ,$$

and

$$2x+2y = b\ .$$

Therefore,

$$x = \frac{1}{7}(2a+b)\ ,$$

and

$$y = \frac{1}{2}(b-2x)\ .$$

The calculated volumes of both of the residue and the oxygen consumption which are shown in brackets in the table agree well with the corresponding observed values.

Discussion. Although carbon monoxide is found in considerable proportion in all cases in this experiment, it was not the case in Kolbe's reaction or one related to it which are generally known in the literature, as seen from the following illustrations. Ammonium and potassium acetates were electrolysed by R. Matsuda and his collaborators⁽⁵⁾ and in both cases 1% at most carbon monoxide was produced.

H. Hofer and M. Moest⁽⁶⁾ obtained an anodic gas which consisted of carbon dioxide and ethane by electrolysing sodium acetate in the presence of sodium perchlorate, but nothing was mentioned about either oxygen or carbon monoxide. According to the same authors electrolyses of sodium acetate in the presence of sodium sulphate, and also of potassium acetate in the presence of potassium bicarbonate resulted in very little carbon monoxide production.

R. E. Gibson⁽⁷⁾ obtained an anodic gas which consisted of 87% carbon dioxide, 3% carbon monoxide, 9% oxygen and 1% methane by electrolysing a mixture of 20 c.c. concentrated sulphuric acid, 100 c.c. acetic anhydride and 5 c.c. water. O. J. Walker and G. L. E. Wild⁽⁸⁾ stated

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(5) R. Matsuda and his collaborators, (1), (2).
(6) H. Hofer and M. Moest, *Ann.*, **323** (1902), 284.
(7) R. E. Gibson, *J. Chem. Soc.*, **127** (1925), 483.
(8) O. J. Walker and G. L. E. Wild, *ibid.*, **1935**, 207.

that decomposition of acetyl peroxide produced a gaseous mixture which contained 1% carbon monoxide. The present writers electrolysed oxalic acid: the anolyte was the saturated solution (0.29N) of oxalic acid in 10 N sulphuric acid, and the catholyte 6 N sulphuric acid (vide Fig. 2). At $D_A=0.10$ amp./cm^2., the anodic gas was nearly of the same composition as that of the anolyte No. 1, but at $D_A=0.30$ and 0.50 amp./cm^2. it was not. Though it will be interesting to compare the nature of acetic acid in sulphuric acid solution towards the anodic action with those of other substances in order to study the mechanism by which carbon monoxide is formed, further experiments are reserved for another occasion.

Walker and Wild obtained a gaseous mixture by decomposing acetyl peroxide which consisted of 27–40% methane, 55–64% carbon dioxide, ca. 9% oxygen, and ca. 4% ethane. S. Glasstone and A. Hickling⁽⁹⁾ studied the reaction between barium peroxide and acetic anhydride with and without water which, in both cases, produced a gesous mixture which consisted of 65.9% carbon dioxide, 6.1% oxygen, 12.0% methane and 6.1% ethane. These are the reasons why they can not agree with the peroxide theory as the mechanism of Kolbe's reaction. The above two cases of decomposition of acetyl peroxide, however, are under very different conditions from that which will take place at a platinum-anode.

It was proposed already in Parts V, VI, and VII that the peroxide theory which assumes acetyl peroxide as the intermediate to produce ethane is preferable to other mechanisms, and it has been assumed in the present work that a gas which has a chemical formula $(CO_2)_2$, is formed by the anodic reaction. Now if ethane be produced by the decomposition of acetyl peroxide it will not be impossible that this new substance is formed as a by-product, as in the following equation:

$$(CH_3COO)_2 = C_2H_6 + (CO_2)_2 \ .$$

Though the existence of $(CO_2)_2$ has to be confirmed by further tests from different angles, it seems to the present writers that it is a new evidence for the peroxide theory, if it exists at all.

The writers wish to express their heartfelt thanks to Prof. Motooki Matsui, D. Sc., for his unfailing encouragement. Thanks are also due to the Department of Education for a grant (Kwagaku Kenkyu Hi) for the sake of the present work.

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(9) S. Glasstone and A. Hickling, *J. Soc. Chem. Ind.*, **53** (1934), 512.