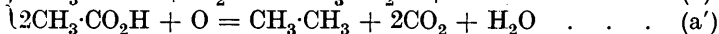
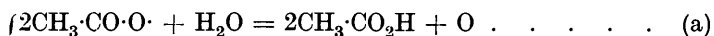


CCCCXVIII.—*The Mechanism of Kolbe's
Electrosynthesis.*

By DAVID ALEXANDER FAIRWEATHER and OSWALD JAMES WALKER.

SINCE Kolbe's discovery of the production of ethane at the anode during the electrolysis of a solution of potassium acetate (*Annalen*, 1849, 69, 279), many investigations have been made with a view to determine the nature of the undoubtedly complex process involved. Two rival theories have emerged: (1) The "oxidation" theory, which supposes that all the discharged anions react with water to give the acid, which is then oxidised by atomic oxygen to the synthetic product; and (2) the "discharged ion" theory, which supposes that two discharged anions unite directly. The following equations represent these reactions:



In two recent contributions to this subject (Gibson, J., 1925, 127, 475; Robertson, *ibid.*, p. 2057) it is claimed that the oxidation theory has been proved to hold, not only for the ethane synthesis, but also for the Crum Brown and Walker synthesis of dibasic acids. The conclusions drawn in these papers do not seem to be entirely sound, and, moreover, fresh experimental evidence has now been obtained which demonstrates beyond all doubt that synthesis is due solely to the direct interaction of the discharged ions.

Concerning the intrinsic probability of the oxidation theory, it must be admitted that it would be somewhat surprising if the carboxylic hydrogen atom of a fatty acid were attacked by an oxidising agent in preference to the hydrogen atoms of the hydrocarbon residue, since one is accustomed to regard a carboxyl group as being very stable towards oxidising agents. The oxidation theory, in fact, could scarcely have been considered seriously had it not been shown by Gordon (*J. Physical Chem.*, 1914, **18**, 55) that comparatively large quantities of ethane and methane are formed when acetic acid is oxidised in dilute solution and at a moderate temperature with potassium persulphate.

Referring to the well-established fact that an anode of smooth platinum must acquire a definite potential before any appreciable quantity of ethane is formed, Gibson deduces that at this potential either (a) the acetate ion is first discharged, or (b) the acetic acid, in becoming oxidised to ethane, begins to act as a depolariser. This view requires some modification, since the so-called "discharging potential" of organic anions must, in reality, be a depolarisation potential. It may be assumed that the first reaction at the anode, *viz.*, the neutralisation of the electric charges on the ions, takes place with infinite velocity. Any subsequent chemical reactions in which the discharged ions may be involved, will, however, take place with a finite velocity dependent on the concentration of the reacting substances and on the temperature. Thus, no matter what views may be held as to the mechanism of ethane formation, there must necessarily exist in the neighbourhood of the anode an accumulation of the unstable substance $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot$. Some at least of these discharged ions react with water, giving atomic oxygen. We thus have two unstable products at the anode, either of which may cause a back *E.M.F.* The point in the anode potential-current curve at which the current begins to increase rapidly is therefore the point at which these substances have attained concentrations sufficiently high to allow of their being removed with appreciable rapidity. This depolarisation may conceivably be effected in five ways :

- (1) $\text{O} + \text{O} = \text{O}_2$.
- (2) $2\text{CH}_3\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$.
- (3) $\text{CH}_3\cdot\text{CO}_2\text{H} + 4\text{O} = 2\text{CO}_2 + 2\text{H}_2\text{O}$.
- (4) $2\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot + 7\text{O} = 4\text{CO}_2 + 3\text{H}_2\text{O}$.
- (5) $2\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot = \text{CH}_3\cdot\text{CH}_3 + 2\text{CO}_2$.

Gibson's second alternative is therefore capable of extension, and his conclusion that the particular reaction studied, *viz.*, the formation of trichloromethyl trichloroacetate, is an oxidation reaction

can scarcely be held as valid, since it is largely based on the fact that the potential at which this ester was observed to be first formed is not the discharging potential of the trichloroacetate ion.

Both Gibson and Robertson record a sharp fall in the amount of oxygen evolved in unit time at or about the synthetic potential, and entirely upon this evidence Robertson bases his conclusion that the synthesis of ethyl succinate is an oxidation reaction (*loc. cit.*, p. 2064). Such a fall was not observed by us. In any case, if equations (a) and (a') be added together, equation (b) is obtained, *i.e.*, the amount of oxygen liberated must be independent of the mode of ethane formation. On either theory, the net result evidently is that one molecule of ethane is produced from two discharged ions without either liberating or using up any oxygen. The amount of evolved oxygen depends on the concentration of active oxygen at the anode, since it is produced by the reaction $O + O = O_2$. If with rising anode potential the amount of oxygen evolved in unit time decreases, the concentration of atomic oxygen must also be decreasing; but since the anode potential is rising, it cannot be the atomic oxygen alone which is responsible for the back *E.M.F.* observed—this must also be due to the discharged ions themselves.

Since the oxidation theory involves the partial oxidation of the acid, it is of interest to inquire to what extent complete oxidation to carbon dioxide and water takes place. Murray (J., 1892, **61**, 34) pointed out that the readiness with which complete oxidation takes place is inconsistent with the oxidation theory. From Robertson's figures it may be shown that about 30 to 40% of the oxygen developed at the anode is used for complete oxidation between the potentials of 2.02 and 2.30 volts, *i.e.*, before any synthesis commences. This theory therefore requires the extremely unlikely assumption that partial oxidation necessitates a higher potential (and therefore greater concentrations of reacting materials) than complete oxidation.

No positive evidence whatever would therefore appear to have been put forward in support of the oxidation theory. On the other hand, the recent work of Salauze (*Bull. Soc. chim.*, 1925, **37**, 522), who obtained good yields of ethane by electrolysis of a methyl-alcoholic solution of an acetate, proves that under these conditions the discharged ions do indeed interact directly.

In order to collect further data bearing upon the phenomenon of electrosynthesis, the electrolysis of solutions of acetates and propionates has been studied with regard to the effect of concentration and temperature of the solution, current density, anode potential, nature of solvent, and material of anode.

E X P E R I M E N T A L.

The apparatus used was of the same type as that employed by Gibson and by Robertson. The anode and cathode gases were collected together and transferred to a Bone and Wheeler gas-analysis apparatus by means of a Dittmar pipette filled with mercury. A complete analysis of each gas sample was made. The potentials given are on the hydrogen standard, and were obtained by calculation after direct comparison with a normal calomel electrode.

Experiments with Solutions of Potassium Acetate.—All acetate solutions were made *N* with respect to the free acid to prevent the solution becoming alkaline during the course of an experiment. *N*-Potassium acetate solution was electrolysed, three anodes of smooth platinum of different sizes being used with the same smooth platinum cathode. From Fig. 1 it will be seen that the values of *C.D.* and anode potential for all three anodes can be represented on one smooth curve, and that the ratio of ethane to hydrogen increases regularly with increasing anode potential independently of the size of the anode. Murray states (*loc. cit.*, p. 25) that "although the yield of ethane is increased by increasing the current or by employing a smaller anode, the variation is not to be accounted for by a change in current density alone. There are apparently some other factors influencing the electrolysis." The factor which Murray neglected appears to be the anode potential: between the limits of 2.7 volts, below which no formation of ethane takes place, and 3.0—3.1 volts, above which the yield of ethane can no longer be increased, the amount of ethane formed does increase with the *C.D.* When, however, the ethane:hydrogen ratio has reached its maximum value of nearly 0.9, the *C.D.* can be increased enormously without affecting the yield of ethane.

An increase in the concentration of the electrolyte scarcely affects the formation of ethane above 2.7 volts, as will be seen from the data obtained with a 3*N*-solution, which are shown graphically in Fig. 2. Ethane formation takes place, however, at somewhat lower anode potentials the more concentrated the solution, as is shown in Table I.

TABLE I.

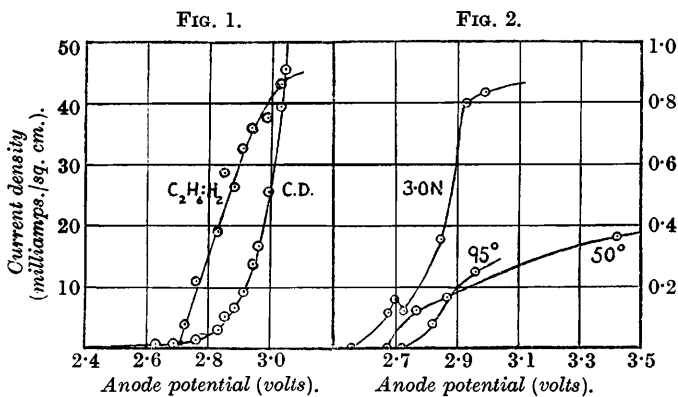
Concentration	3 <i>N</i>	4 <i>N</i>	5 <i>N</i>
Anode potential	2.68	2.66	2.62
C ₂ H ₆ : H ₂	0.11	0.11	0.12

The values of *C.D.* and of the ethane:hydrogen ratio for the two concentrations of acetate have been plotted against one another in Fig. 3. Up to *C.D.*'s of about 20 milliamp./sq. cm. the ratio

increases rapidly. These results indicate that a certain minimum concentration of discharged ionic products is necessary before any appreciable formation of ethane takes place.

A *N*-solution of potassium acetate was also electrolysed at 50° and 95°, the electrolysis cell being immersed in thermostats kept at these temperatures: an increase in temperature did not greatly influence the *P.D.* at which ethane formation commenced; as will be seen, however, from Fig. 2, the amount of ethane formed is less at the higher temperatures.

Experiments with Solutions of Potassium Propionate.—Preuner and Ludlam (*Z. physikal. Chem.*, 1907, **59**, 682) showed that with a 0.5*N*-solution of potassium propionate a polished platinum anode must acquire potentials of 2.58 volts and 2.70 volts, referred to a



(The right-hand scale of ordinates represents the ratio $C_2H_4 : H_2$ and relates to both diagrams.)

hydrogen electrode in the same solution as standard, for ethylene and butane formation, respectively. It seemed desirable to ascertain the effect of other factors on the products of electrolysis. All solutions were *N* with respect to free propionic acid.

N-Potassium propionate solution was electrolysed with smooth platinum electrodes. At low anode potentials, the gases evolved consisted mainly of hydrogen and oxygen with a little ethylene, but no butane. As the *P.D.* was raised the ethylene increased rapidly, reaching a maximum, after which butane made its appearance. Simultaneously with the increase of ethylene, the oxygen began to decrease, finally reaching a minimum. About 1% of carbon monoxide was always present. The results obtained with an anode of 7.2 sq. cm. surface are given in Table II. It is seen that the ethylene:hydrogen ratio begins to increase rapidly at 2.60 volts and tends to reach an asymptotic value of about 0.60

at 2.95 volts. Table III shows the results obtained with a 4*N*-solution using the same electrodes. The corresponding curve is of the same shape as with the *N*-solution, but is displaced 0.15 volt to the left, the ethylene formation commencing at a lower potential.

A *N*-solution was also electrolysed at 50°, using a smooth platinum anode of 0.165 sq. cm. surface. From Table IV it is seen that, although there is more ethylene at low potentials at this temperature, the increase with rise of anode potential is more gradual and the ethylene : hydrogen ratio does not increase much beyond 0.4.

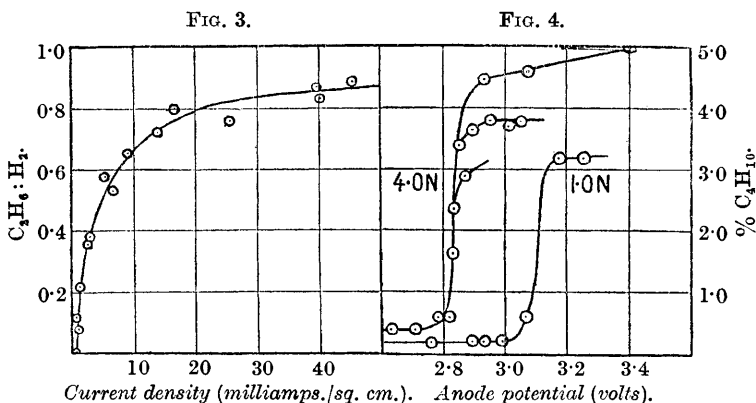


TABLE II.

<i>N</i> -Soln. at 10°. Anode = 7.2 sq. cm.				<i>N</i> -Soln. at 10°. Anode = 7.2 sq. cm.			
<i>A.P.</i>	<i>C.D.</i>	C_2H_4/H_2	O_2/H_2	<i>A.P.</i>	<i>C.D.</i>	C_2H_4/H_2	O_2/H_2
2.36	0.06	0.01	0.23	2.75	2.64	0.24	0.12
2.48	0.08	0.02	0.29	2.78	8.06	0.33	0.067
2.54	0.17	0.01	0.37	2.79	—	0.41	0.043
2.60	0.35	0.04	0.365	2.83	—	0.47	0.030
2.66	0.61	0.07	0.32	2.89	—	0.55	0.022
2.71	0.93	0.13	0.23	2.92	—	0.58	0.024

TABLE III.

4 <i>N</i> -Soln. at 10°. Anode = 7.2 sq. cm.			
<i>A.P.</i>	<i>C.D.</i>	C_2H_4/H_2	O_2/H_2
2.35	0.01	0.01	0.37
2.46	0.07	0.03	0.36
2.54	0.13	0.10	0.30
2.60	0.31	0.29	0.14
2.63	0.82	0.43	0.047
2.71	5.56	0.58	0.018
2.75	8.33	0.59	0.011

TABLE IV.

<i>N</i> -Soln at 50°. Anode = 0.165 sq. cm.			
<i>A.P.</i>	<i>C.D.</i>	C_2H_4/H_2	O_2/H_2
2.56	2.7	0.04	0.28
2.63	6.1	0.09	0.24
2.68	12.1	0.16	0.17
2.75	28.5	0.25	0.10
2.79	46.1	0.28	0.077
2.86	84.8	0.34	0.055
2.95	158.2	0.38	0.042
3.07	249.7	0.40	0.031
3.15	304.2	0.41	0.029

Complete oxidation is, on the whole, more vigorous at 50° and also more free oxygen is evolved above 2.75 volts than at 10°. It appears that the increase of temperature increases the rate of reaction of the discharged ions with water more than it increases the rate of their interaction.

Fig. 4 shows the relation between the anode potential and the percentage of butane (after removal of carbon dioxide) for the two concentrations. With *N*-solution, butane begins to be formed in appreciable quantity at 3.05 volts and reaches a maximum of 3.2% at 3.15 volts. No greater quantity was obtained with *P.D.*'s up to 4.6 volts. With 4*N*-solution, three anodes were used, in order to cover the desired range of *C.D.*'s. The amount of butane increases suddenly at about 2.8 volts and reaches a maximum of 5.0% with the smallest anode. At 50°, no butane was formed even at high potentials.

Nature of the Anode Material.—A phenomenon which is somewhat difficult to explain is the profound influence of the anode material on synthesis in aqueous solution. In confirmation of the work of Preuner and Ludlam (*loc. cit.*, p. 689), it was found that at platinised platinum anodes no synthesis occurred with solutions of potassium acetate and of potassium propionate, although the presence of up to 10% of carbon dioxide showed that complete oxidation had taken place. With very large *C.D.*'s, small quantities of ethane and ethylene were obtained from the acetate and propionate solutions, respectively. In these cases, however, some of the platinum black had become detached and small spots of bright platinum were visible.

With gold anodes, we could detect no trace of synthetic product. With a *N*-solution of potassium acetate, the current increased regularly with increasing anode potential, whilst the gas evolved at 3.1 volts still consisted of hydrogen and oxygen with about 3% of carbon dioxide. The propionate solution gave a gas of similar composition at *P.D.*'s between 3 and 5.3 volts. The anode suffered considerable disintegration, and the solution became brown with dispersed gold.

Fichter and Krummenacher (*Helv. Chim. Acta*, 1918, **1**, 148) suggested that the ability of a metal to promote the Kolbe synthesis was connected with its oxygen overvoltage, and Gibson (*loc. cit.*, p. 484) also discusses this view. It seems more reasonable, however, to approach the problem from the point of view adopted by Preuner and Ludlam. The discharged ions may be supposed to react either with water to give acid and oxygen or with themselves to effect synthesis. Synthesis cannot occur unless there is a sufficient concentration of discharged ions at the anode. We are thus led to

the conclusion that the velocity of the reaction of discharged ions with water at surfaces of platinised platinum and of gold is much greater than at one of smooth platinum, so that their concentration does not attain a value sufficiently high to give synthesis.

Experiments with Non-aqueous Solvents.—The nature of the anode would be expected to have little effect when the solvent is such that reaction with the discharged ions cannot take place. Hofgartner (*Monatsh.*, 1911, **32**, 523) obtained ethane : hydrogen ratios as high as 0.97 by electrolysing an 8.8% solution of potassium acetate in glacial acetic acid with a smooth platinum anode. With the same anode material, Salauze (*loc. cit.*) obtained by electrolysis of acetates in methyl-alcoholic solution 95% of the possible ethane, and showed that in this solvent the nature of the anode, provided that it is not attacked, has much less influence than in aqueous solution.

The following experiment shows the effect of the addition of water on the electrolysis of 4.9 g. of potassium acetate and 1.52 g. of acetic acid in 100 c.c. of methyl-alcoholic solution. A platinised platinum anode of 0.165 sq. cm. surface and a smooth platinum cathode were used, and the current was maintained at the constant value of 25 milliamp. in each determination.

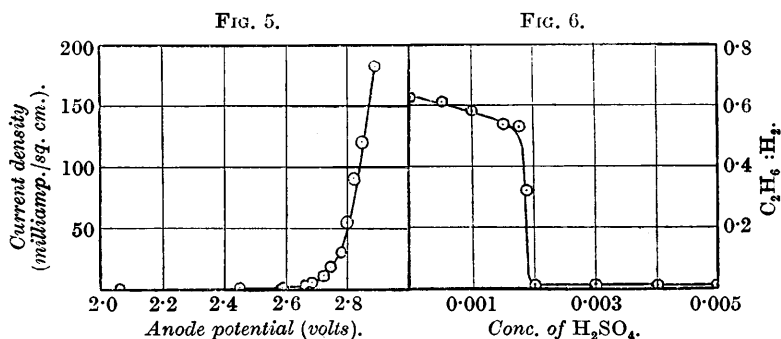
CH ₃ OH (c.c.)	100	95	90	80	0
H ₂ O (c.c.)	0	5	10	20	100
C ₂ H ₆ /H ₂	0.71	0.58	0.22	0	0

It will be seen that ethane formation is inhibited by the presence of water. The way in which the effect due to the anode material is dependent on the solvent is further shown by electrolysing a solution of anhydrous sodium acetate in glacial acetic acid with an anode of (1) smooth platinum and (2) gold. The ratios of ethane to hydrogen in the evolved gases were 0.86 and 0.77, respectively. Synthesis therefore takes place readily at a gold anode in this solvent.

It has been shown that the yield of butane from the electrolysis of aqueous solutions of potassium propionate is very small. By using an anhydrous solvent, however, much better yields can be obtained. A *N*-solution of potassium propionate in equal volumes of methyl alcohol and propionic acid was electrolysed with a smooth platinum anode at 100 milliamp. until the liquid was saturated with the gases, which were then found in the following proportions : C₂H₄, 12.3; C₄H₁₀, 36.0; O₂, 0.5; CO, 0.5; H₂, 50.7%. A similar experiment with a gold anode gave a gas of approximately the same composition. It need scarcely be pointed out that this constitutes a valuable method for the preparation of butane.

We have stated that the bends in current-anode potential

curves must be due to depolarisation. Now in anhydrous solution this depolarisation must be effected exclusively by union of the discharged ions to give synthesis. It was therefore considered of interest to examine the electromotive phenomena at the anode under these conditions, and potential-current density curves were constructed for a smooth platinum anode in a methyl-alcoholic solution of potassium propionate (N) and propionic acid (N), care being taken to exclude traces of water. The propionate solution itself was used as a buffer solution between the cell and the potassium chloride solution leading to the calomel electrode. As shown in Fig. 5, depolarisation evidently occurs at 2.6—2.7 volts. Owing to the great solubility of the gases in methyl alcohol, it was not possible to obtain for analysis representative samples at the various anode potentials.



The Electrolytic Oxidation of Acetic Acid.—It might be held that, although the discharged ions interact in non-aqueous solutions, synthesis in aqueous solutions may be due either partly or entirely to oxidation of the free acid. It was thought that if in a solution of acetic acid the acetate ions could be prevented from discharging, whilst at the same time the oxidation conditions were maintained unaltered, it would be possible to ascertain conclusively whether or no ethane is obtained by oxidation of the acid. These conditions have been realised in the following experiment. A concentrated aqueous solution of acetic acid ($15N$) was electrolysed with the addition of varying small quantities of sulphuric acid, smooth platinum electrodes being used and a constant current of 35 milliamp. Each electrolysis was allowed to proceed for about 24 hours to ensure saturation of the liquid with the gases evolved.

The results are shown graphically in Fig. 6, in which the ethane : hydrogen ratio is plotted against the concentration of sulphuric acid in g.-equiv. per litre. It will be seen that the critical concentration of sulphuric acid is $0.002N$, and that the formation of

ethane is then almost completely prevented. This concentration evidently corresponds to a critical concentration of discharged acetate ions, below which synthesis cannot take place. The ionisation of the acetic acid, already small owing to the high concentration of the solution, is still further reduced by the sulphuric acid; the current is then partly carried by the SO_4'' and HSO_4' ions. These, after discharge, react with water to give atomic oxygen, which, however, does not oxidise the acetic acid to ethane. Little oxygen was evolved in any of the experiments; it was used up in oxidising the acetic acid to carbon dioxide and water, 20—25% of carbon dioxide being present even in absence of ethane. This experiment shows beyond doubt that ethane is produced by the interaction of discharged acetate ions, and that electrolytic oxygen, when it oxidises acetic acid, does so completely and not partly.

Conclusion and Summary.

It is shown, both by a consideration of the work of previous investigators and by the presentation of fresh experimental evidence, that the phenomena observed in the electrolysis of solutions of fatty acids can only be accounted for on the "discharged ion" theory as originally proposed by Crum Brown and Walker. The reactions in which the discharged ions take part may now be formulated as follows :

1. $2\text{R}\cdot\text{CO}\cdot\text{O}\cdot + \text{H}_2\text{O} = 2\text{R}\cdot\text{CO}_2\text{H} + \text{O}$ (Faraday reaction).
2. $2\text{R}\cdot\text{CO}\cdot\text{O}\cdot = \text{R}\cdot\text{R} + 2\text{CO}_2$ (Synthetic reaction).
3. $2\text{R}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot = \text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + (\text{R} - \text{H})\cdot\text{CH}_2 + \text{CO}_2$ (Unsaturated product).
4. $2\text{R}\cdot\text{CO}\cdot\text{O}\cdot = \text{R}\cdot\text{CO}_2\text{R} + \text{CO}_2$ (Ester formation).
5. $\text{R}\cdot\text{CO}\cdot\text{O}\cdot + \text{OH} = \text{R}\cdot\text{OH} + \text{CO}_2$ (Alcohol formation).
6. $\text{R}\cdot\text{CO}\cdot\text{O}\cdot + n\text{O} = x\text{H}_2\text{O} + y\text{CO}_2$ (Complete oxidation).

The conditions which favour reactions 2 and 3 are precisely those which retard or prevent reaction 1.

The main points which have been put forward in support of the above theory may be summarised as follows :

1. The arguments advanced by Gibson and by Robertson in favour of the oxidation theory are largely fallacious.
2. The electrolytic oxidation of acetic acid has been shown to be complete and not partial under ordinary conditions. Complete oxidation takes place to a considerable extent at low anode potentials.
3. The presence of a definite concentration of the discharged anions themselves is indispensable for synthesis.
4. In confirmation of the results of other workers, it has been

shown that synthesis can and does take place in non-aqueous solutions to which the oxidation theory is not applicable.

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UNIVERSITY OF EDINBURGH.

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