414. Studies in Electrolytic Oxidation. Part VI. The Anodic Oxidation of Acetates: The Mechanism of the Kolbe and the Hofer–Moest Reaction in Aqueous Solution.

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IN recent years two theories of the mechanism of the formation of ethane at the anode in the electrolysis of acetate solutions have been maintained. Brown and Walker's original theory (*Annalen*, 1891, **261**, 107) that the process consisted in the discharge of two acetate ions, followed by interaction of the radicals, $2CH_3{\cdot}CO_2' = 2CH_3{\cdot}CO_2 + 2e$, $2CH_3{\cdot}CO_2 = C_2H_6 + 2CO_2$, has been particularly supported, although with some qualification, by Walker and his co-workers (see, *e.g.*, Fairweather and Walker, J., 1926, 3111; Walker J., 1928, 2040; Shukla and Walker, *Trans. Faraday Soc.*, 1931, **27**, 35, 722; 1932, **28**, 457), whereas the view that the reaction is a chemical one has been urged, mainly by Fichter and his associates (*e.g.*, *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 131; *J. Soc. Chem. Ind.*, 1929, **48**, 347; see also Gibson, J., 1925, **127**, 475), who consider that oxidation by active oxygen leads to acetyl peroxide, which then decomposes with the formation of the characteristic electrolytic products. Both theories are inadequate in that they fail to account for the predominating influence of the nature of the anode material on the formation of ethane in aqueous solution, and for the supersession of the Kolbe synthesis by the Hofer–Moest reaction (*Annalen*, 1902, **323**, 284), *i.e.*, formation of methyl alcohol, under certain conditions; nor will the theories account for observations described in the present work.

In view of the success of the theory developed in the preceding parts of this series (J., 1932, 2345, 2800; 1933, 829; this vol., p. 10) in accounting for electrolytic oxidation phenomena, the action of catalysts for hydrogen peroxide decomposition upon the Kolbe reaction has now been investigated. The electrolysis of acetates and of acetic acid has been studied with smooth and platinised platinum, gold, nickel, and carbon anodes under a variety of conditions, and the results used to throw light on the mechanisms of the reactions involving the anodic formation of ethane and methyl alcohol.

EXPERIMENTAL.

The electrolytic apparatus used differed from that employed by previous workers. It consisted of a cylindrical glass jar (8 cm. diam. and 10 cm. high) fitted with a rubber stopper through which passed a thermometer, a glass stirrer, a tube attached to a glass reservoir for electrolyte, a filter " candle " forming the cathode compartment, a gas-delivery tube with tap, and a wide tube to take a separate rubber stopper carrying the anode. The spindle of the stirrer (30 cm. long) was surrounded by a closely fitting glass tube, so that the liquid in the cell acted as a seal and prevented the escape of gas. The capacity of the jar and associated reservoir was about 500 c.c. The gas-delivery tube led to a nitrometer, used for measuring the volume of the gas evolved. The anode was, in general, a smooth platinum spiral of 2 sq. cm. area, and pressed closely to it was a siphon leading to a calomel cell. Previous to use, the anode was cleaned with concentrated hydrochloric acid, warm concentrated nitric acid, water, heated to redness, and conditioned as described previously (J., 1932, 2347). The cathode was a short platinum wire, and the catholyte was, in general, the same as the anolyte; the cathode gas was not collected. The anolyte was introduced through the glass reservoir, and at the beginning of each electrolysis the jar was completely filled with solution. After electrolysis the gas evolved was displaced into the nitrometer filled with mercury, and its volume measured. Unless otherwise stated, the electrolyte was stirred vigorously during electrolysis by the glass stirrer rotating at 660 r.p.m. Prior to electrolysis, the solution was saturated by passage of carbon dioxide for 1 hour, and a preliminary electrolysis of 300 coulombs was then carried out and the gas rejected. The sample for analysis was usually collected during the passage of 130 coulombs, and after its volume had been measured in the nitrometer, it was transferred to a Bone–Newitt apparatus for analysis. All electrolyses were carried out at room temperature, *i.e.*, about 20°.

A complete gas analysis was carried out in almost all cases: carbon dioxide was absorbed by potassium hydroxide, oxygen by alkaline pyrogallol, ethylene by bromine in potassium bromide solution, carbon monoxide by ammoniacal cuprous chloride, hydrogen by colloidal palladium in sodium picrate solution at 60° (see Beet, *Fuel*, 1928, **7**, 44), and methane and ethane were finally determined by explosion with excess oxygen. The last estimation was shown by MacGillivray to be accurate provided certain precautions are observed (J., 1932, 941), and experience in the present work entirely confirms this.

The results of the electrolyses are expressed as current efficiencies of ethane formation, calculated from the volume of gas evolved and its determined ethane content; where there is any particular feature of interest the analysis of the gas is also given. Some workers have relied upon the analysis of the gas alone for illustrating their results, but this is by no means satisfactory. Fluctuations in the amount of carbon dioxide frequently occur owing to the difficulty of maintaining constant saturation of the electrolyte with this gas, and so there are corresponding changes in the ethane content of the gas analysed; the current efficiency of ethane formation is, however, independent of this factor and is reproducible. Since the formation of ethane is accompanied by much more carbon dioxide than can arise for an equal quantity of electricity in any other oxidation process, a considerable fall in efficiency of ethane production may appear as only a small change in the analytical figures; this is a further disadvantage of the use of the gas analysis as sole guide in the study of the oxidation.

Results.

General Factors.—To determine the effect of duration of electrolysis and to investigate the reproducibility of the results, a solution of *N*-potassium acetate and *N*-acetic acid was electrolysed at a *C.D.* of 0·25 amp./sq. cm., samples being collected after the passage of 300, 1330, and 2360 coulombs. In two sets of experiments the following results were obtained for the efficiency of ethane formation: (1) 89, 90, 88; (2) 89, 91, 89%. It is seen that if other factors remain constant, duration of electrolysis itself has no influence on the efficiency. The results are in general reproducible to 1—2%.

The effect of variation of *C.D.* is shown by the following data obtained for the electrolysis of *N*-potassium acetate and *N*-acetic acid:

C.D., amp./sq. cm.	0·5	0·25	0·05	0·025	0·005
Efficiency, %	89	89	77	71	52

The results produced by change of concentration of acetate are illustrated below, the *C.D.* being 0·05 amp./sq. cm.

KOAc, *N*	4	2	1	0·5	0·1
HOAc, *N*	4	2	1	0·5	0·1
Efficiency, %	76	77	77	64	44

In confirmation of the results of previous workers, it is seen that decrease of *C.D.* or of acetate concentration below certain values results in a rapid decrease of the efficiency of ethane formation.

The effect of varying the proportions of potassium acetate and acetic acid while the total acetate concentration is kept constant is shown below, a *C.D.* of 0·05 amp./sq. cm. being used.

KOAc, *N*	2	1·5	1·0	0·5	0
HOAc, *N*	0	0·5	1·0	1·5	2
Efficiency, %	67	70	77	74	71

It is seen that a maximum efficiency is obtained with an electrolyte consisting of equimolar parts of the salt and acid, but that this maximum is rather flat.

In all the experiments the gas evolved was mainly carbon dioxide and ethane, with small amounts of methane (0·4—4·0%) and oxygen (0·5—1·2%), and traces of ethylene, carbon monoxide, and hydrogen.

Influence of Catalysts for Hydrogen Peroxide Decomposition.—The catalysts were introduced in the form of metallic acetates into a potassium acetate and acetic acid electrolyte, so that the resulting solution was *N* with respect to acetate and *N* with respect to acetic acid. Two sets of experiments were carried out with *C.D.*'s of 0·025 and 0·25 amp./sq. cm. severally. In some cases the gas samples had to be collected during the passage of 300 instead of 130 coulombs in order to obtain sufficient gas for manipulation. Some solid catalysts were also used: the manganese dioxide and cobaltic oxide were introduced as fine powders; they dissolved very slightly in the electrolyte. The silver was prepared by precipitation with zinc; it did not dissolve in the acetate mixture. The animal charcoal was purified and activated by the method of Firth and Watson (*Trans. Faraday Soc.*, 1924, **20**, 370). 2 G. of each of these solid catalysts were introduced into 500 c.c. of electrolyte. The efficiencies and analyses are given in Table I.

TABLE I.

Effect of Catalysts for Hydrogen Peroxide Decomposition.

Catalyst.	Efficiency, %, for ethane.	Analysis of gas, %.							n.
		CO_2.	O_2.	C_2H_4.	CO.	H_2.	C_2H_6.	CH_4.	
			C.D., 0·025 amp./sq. cm.						
(None)	71	67·7	0·6	0·4	0·4	0·1	29·4	1·4	—
Mn 0·010*M*	10	86·9	1·5	0·2	0·5	0·2	7·3	1·0	1·7
0·002*M*	52	75·8	0·5	0·2	0·3	0·0	20·9	1·7	—
Pb 0·001*M*	0	75·8	22·6	—	—	—	0·3	0·1	1·9
Ag 0·020*M*	0	81·2	17·4	—	—	—	0·4	—	—
0·001*M*	2	73·3	22·8	—	—	—	2·6	—	1·7
Cu 0·05*M*	12	84·4	3·4	0·2	0·5	0·1	10·1	0·9	2·0
Co 0·05*M*	9	70·9	16·3	0·2	0·7	0·2	10·1	0·3	2·9
Fe 0·02*M*	56	77·9	0·3	0·3	0·3	0·1	19·6	0·9	—
MnO_2	44	73·9	0·7	0·2	0·4	0·2	24·3	—	—
Co_2O_3	65	73·9	0·6	0·3	0·2	0·1	23·1	1·4	—
Ag	63	65·1	1·1	0·2	0·2	0·1	31·1	0·9	—
C	67	74·0	0·5	0·2	0·3	0·0	23·1	1·7	—
			C.D., 0·25 amp./sq. cm.						
(None)	89	66·0	0·6	0·3	0·2	0·1	32·4	0·4	—
Mn 0·10*M*	0	71·7	15·8	0·0	6·7	0·2	0·8	1·6	—
0·05*M*	6	83·4	6·0	0·2	3·0	0·2	5·1	0·9	—
0·01*M*	58	74·3	0·6	0·2	0·2	0·1	23·3	0·4	—
Pb 0·010*M*	2	69·8	25·8	0·1	0·5	0·3	1·8	0·9	—
0·001*M*	59	74·1	0·8	0·2	0·2	0·2	22·9	0·8	—
Ag 0·02*M*	2	60·9	35·5	—	—	—	3·1	—	—
Cu 0·10*M*	33	81·1	1·2	0·2	0·3	0·0	16·7	0·0	—
0·05*M*	55	75·1	0·6	0·1	0·4	0·1	22·6	1·3	—
Co 0·10*M*	61	75·7	0·6	0·3	0·1	0·1	22·4	0·9	—
0·05*M*	72	68·3	0·2	0·3	0·3	0·0	28·8	0·8	—
Fe 0·02*M*	77	70·0	0·4	0·2	0·2	0·2	28·3	0·6	—

It is seen that, in the presence of catalysts for hydrogen peroxide decomposition, ethane formation is greatly decreased and in some cases entirely inhibited. The effects are particularly marked at the lower *C.D.* The solid catalysts do not appear to have such great effects as those introduced as metallic salts. In general, the catalysts increase the carbon dioxide content of the gas evolved; sometimes the amount of oxygen is also raised, particularly in the presence of lead and silver salts. The amount of carbon monoxide is also often increased slightly, and it is of interest that the methane/ethane ratio is frequently increased.

Since these catalysts decrease the efficiency of ethane formation, it becomes of interest to identify the products of the oxidation. This can best be done by determining the quantity of electricity used in producing the carbon dioxide, other than that accompanying the ethane formation. If the alternative to the Kolbe reaction is complete oxidation of the acetic acid to carbon dioxide and water, $CH_3\cdot CO_2H + 4O = 2CO_2 + 2H_2O$, each mol. of this gas will be produced at the expense of 4 faradays of electricity; if the oxidation is not complete, but leads to formation of some other organic product, less than 4 faradays will be required. If x is the % of carbon dioxide in the electrolytic gas after the deduction of the amount accompanying the Kolbe formation of ethane, v is the total volume of gas at N.T.P., Q is the quantity of electricity passed in coulombs, and E is the efficiency of formation of ethane and oxygen, then the number of faradays used in the production of 1 mol. of carbon dioxide by alternative oxidation is given by $n = (100 - E)Q2240/9654vx$. The values of n in a number of reliable cases, in which both the amounts of ethane and oxygen are small, are included in Table I; it is seen that, in general, approximately 2 faradays are required for the production of each mol. of carbon dioxide. This result suggests that the process $CH_3\cdot CO_2H + O = CH_3\cdot OH + CO_2$ is occurring in place of the Kolbe reaction, and so methyl alcohol should be present after electrolysis. In order to detect this substance, it is necessary to electrolyse the solution for an appreciable time, and then further oxidation tends to reduce the total amount formed. From the work of Hofer and Moest (*loc. cit.*), it appeared that the methyl alcohol was most likely to be obtained in quantity by using a rapidly rotating gauze anode, and an electrode of this type, 50 sq. cm. in area, was employed with a current of 2·5 amp.; 400 c.c. of electrolyte were used, and the current passed for 100 minutes. After electrolysis, the solution was made alkaline with sodium carbonate, 100 c.c. were distilled off, and the methyl alcohol in the distillate estimated colorimetrically by Wright's method (*Ind. Eng. Chem.*, 1927, **19**, 750). With a solution containing *N*-acetic acid, *N*-potassium acetate, and 0·02*M*-manganese, the yield of alcohol was 0·4 g., corresponding to a current efficiency of 16%, whereas in a control experiment in which no manganese salt was present, the efficiency was 3%.

Effect of Catalysts for Hydrogen Peroxide Decomposition on Methane Formation.—Shukla and Walker (*loc. cit.*, 1931) showed that methane generally occurs in the gas from the electrolysis of acetate solutions, and the amount increases as the *C.D.* is lowered and the concentration of acetate increased. Observations in the present work confirm this. From the gas analyses for electrolysis in the presence of catalysts for hydrogen peroxide decomposition, it may be seen that the action of these substances is frequently to raise the methane/ethane ratio, although the total hydrocarbon is considerably decreased. To establish this more definitely, a solution of 4*N*-potassium acetate and 4*N*-acetic acid was electrolysed at a *C.D.* of 0·0025 amp./sq. cm., and then the experiment was repeated in the presence of 0·001*M*-lead acetate; the results are given below:

	Efficiency, %, for ethane.	Analysis of gas, %.						
		CO_2.	O_2.	C_2H_4.	CO.	H_2.	C_2H_6.	CH_4.
No catalyst	17	82·6	0·3	0·2	0·5	0·1	10·2	5·2
0·001*M*-Pb	3	82·2	3·5	0·2	0·2	0·1	6·1	5·5

The result is as expected, the methane/ethane ratio in the first case being 0·51, and in the second 0·90.

Influence of Cations not Catalytically Active.—In order to determine the influence of cations other than those known to have a definite catalytic effect on the decomposition of hydrogen peroxide, a number of metallic acetate solutions were electrolysed in the presence of acetic acid. With the exception of uranyl acetate, for which both the salt and free acid were 0·2*N* and the *C.D.* 0·125 amp./sq. cm., the solutions were all *N* with respect to both the metallic acetate and acetic acid; the *C.D.* used was 0·25 amp./sq. cm., and the following current efficiencies for the formation of ethane were obtained:

Cation	$Na^{\cdot}$	$K^{\cdot}$	$NH_4^{\cdot}$	$Ca^{\cdot\cdot}$	$Sr^{\cdot\cdot}$	$Ba^{\cdot\cdot}$	$Mg^{\cdot\cdot}$	$Zn^{\cdot\cdot}$	$Ni^{\cdot\cdot}$	$UO_2^{\cdot\cdot}$
Efficiency, %	80	89	86	85	82	75	79	71	74	78

The Kolbe reaction takes place in each case with high efficiency, and the difference in behaviour between nickel acetate on the one hand and cobalt acetate (Table I) on the other is very striking.

Influence of Nature of Anode Material.—Foerster and Piguet (*Z. Elektrochem.*, 1904, **10**, 729) showed that platinised platinum gave little ethane in the electrolysis of acetate solutions, and this was confirmed by many subsequent workers. If the low yield is due to catalytic decomposition of hydrogen peroxide by the anode material, it should be possible by poisoning the platinum to increase the amount of ethane obtained. The following current efficiencies were obtained in the electrolysis of a solution of *N*-potassium acetate and *N*-acetic acid with a platinised platinum anode at an apparent *C.D.* of 0·25 amp./sq. cm. in the presence of 0·1*M*-mercuric cyanide, 0·1*M*-potassium cyanide, and 0·1*M*-sodium fluoride.

Poison	None	$Hg(CN)_2$	KCN	NaF
Efficiency, %	3	14	13	10

A more marked effect on the Kolbe synthesis was observed when 0·01*M*-mercuric chloride was added to the platinising solution used for blackening the anode; the resulting electrode gave a current efficiency of 42% for the production of ethane, as compared with 3% for an electrode prepared under exactly the same conditions but in the absence of mercuric chloride. The gas evolved in electrolysis with a platinised anode normally contained a considerable proportion of oxygen, but where the efficiency of ethane formation was increased by the addition of a poison the amount of oxygen was diminished, as the following results show:

	Analysis of gas, %.						
	CO_2.	O_2.	C_2H_4.	CO.	H_2.	C_2H_6.	CH_4.
No poison	70·0	24·0	0·2	2·6	0·1	2·5	0·3
0·1*M*-$Hg(CN)_2$	72·5	12·1	0·1	2·4	0·3	11·0	1·0

Foerster and Piguet (*loc. cit.*) also noted that anodic pre-polarisation favoured the formation of ethane, and this effect, which is of importance in connexion with the theory that hydrogen peroxide plays an essential part in many anodic oxidations, has been verified. A platinised platinum electrode was polarised anodically for 30 minutes in 2*N*-sodium hydroxide with a *C.D.* of 0·25 amp./sq. cm., and then used as anode in a 4*N*-potassium acetate solution at the same *C.D.*; the current efficiency of ethane formation was 36%, whereas a similar electrode which had been cathodically polarised for 17 hours at 0·125 amp./sq. cm. in 2*N*-sodium hydroxide gave an efficiency of only 3% in the same acetate solution.

Experiments were also carried out with gold, nickel, graphite, and arc-carbon anodes, the superficial area in each case being 2 sq. cm. as before; prior to use, the gold and nickel electrodes were cleaned with concentrated hydrochloric acid and water, and the carbon anodes with water alone. *N*-Potassium acetate and *N*-acetic acid was used as electrolyte and the *C.D.* was 0·25 amp./sq. cm. The current efficiencies of ethane formation are given below:

Electrode	Au	Ni	Graphite	Arc C
Efficiency, %	0	0	4	21

The gas evolved with the gold and the nickel anode was mainly carbon dioxide and oxygen, whilst the graphite electrode gave chiefly carbon dioxide with a moderate amount of oxygen. The fair efficiency with the arc-carbon anode confirms Shukla and Walker's observation (*loc. cit.*, 1932), but the soft graphite anode which disintegrated considerably during the electrolysis gave a low efficiency, showing that the state of division of the carbon is important. During electrolysis the gold anode became covered with a brownish-black deposit consisting of gold oxide and finely divided metal, and this was found to bring about a vigorous decomposition of hydrogen peroxide. After use in the electrolysis of dilute sodium hydroxide or in an acetate solution, a nickel anode was observed to be covered with a black deposit, probably nickel peroxide, and on its being introduced into hydrogen peroxide solution there was a vigorous momentary evolution of gas. A specimen of nickel peroxide was prepared by the method of Chirnoaga (J., 1926, 1698) and this reacted vigorously with hydrogen peroxide, evolving oxygen; the reaction is not catalytic, but a mutual reduction, and ceases when the nickel peroxide is reduced. It may be noted that the lower oxides of nickel do not decompose hydrogen peroxide appreciably; consequently, when the potential remains below that at which the peroxide can be formed, electrolytic processes may be carried out efficiently at a nickel anode (see J., 1932, 2804; 1933, 833).

Electrolysis of Acetic Acid Solutions in the Presence of Foreign Anions.—It was formerly believed that a solution of acetic acid itself did not give the Kolbe synthesis, but Matsui and Kizaki (*Mem. Coll. Sci. Kyoto*, 1933, **16**, *A*, 297) showed that ethane could be obtained with high efficiency in the absence of foreign anions; on the addition of an indifferent strong electrolyte such as potassium sulphate, however, the formation of ethane was inhibited. Their experiments were not very extensive and the results were in many cases complicated by change of p_H value of the solution and by oxidation of the added anion. A series of experiments has therefore been carried out in the present work; 2*N*-acetic acid and a *C.D.* of 0·05 amp./sq. cm. with the smooth platinum anode were employed, and the anion was introduced as potassium salt so as to make the solution 0·01*N* in each case. The natures of the salts added were such that the p_H of the acetic acid was not altered appreciably by the addition, nor was oxidation of the added anion likely to take place. The results are given in Table II; for reasons which will appear later, the mobilities of the anions (*l*) and the number of faradays (*n*) required to produce 1 mol. of carbon dioxide, apart from that formed in the Kolbe reaction, are also included. The

TABLE II.

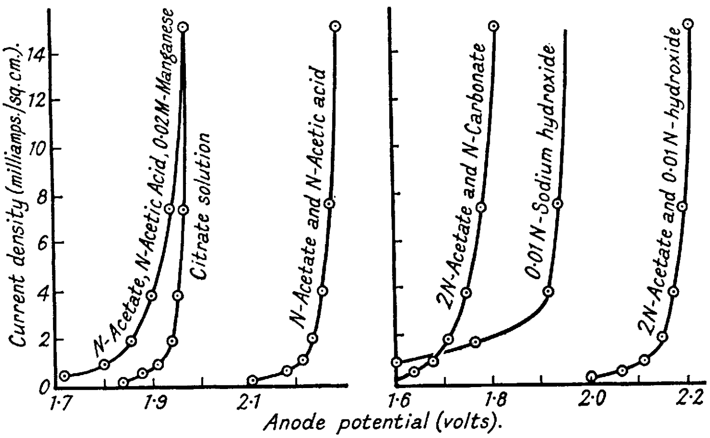
Effect of Anions on the Electrolysis of Acetic Acid.

Salt.	Efficiency, %, for ethane.	Analysis of gas, %.							*l*.	*n*.
		CO_2.	O_2.	C_2H_4.	CO.	H_2.	C_2H_6.	CH_4.		
(None)	71	76·3	0·3	0·2	0·2	0·2	21·3	1·2	—	—
KF	30	81·3	0·9	0·2	0·1	0·2	14·7	2·5	47	1·3
$KClO_4$	20	85·2	0·7	0·1	0·3	0·1	11·4	1·2	64	1·4
KNO_3	19	84·9	0·6	0·1	0·5	0·3	11·8	1·1	62	1·6
KH_2PO_4	17	83·4	0·7	0·1	0·5	0·1	12·4	1·6	—	2·1
KCl	5	89·3	2·0	0·7	1·0	0·5	4·1	1·0	65	1·9
K_2SO_4	3	93·0	1·8	0·1	0·0	0·3	2·9	—	69	2·4
$K_3Fe(CN)_6$	0	91·3	7·2	—	—	—	0·4	0·2	97	2·6

addition of a weak electrolyte such as boric acid was found to have no effect on the Kolbe reaction; *e.g.*, with a solution of 2*N*-acetic acid and 0·01*M*-boric acid, the efficiency of ethane formation was 72%. In the presence of potassium acetate the effect of the anions was small unless they were present in considerable concentration : for instance, with *N*-potassium acetate, *N*-acetic acid, and a *C.D.* of 0·05 amp./sq. cm. the efficiency of ethane formation was reduced from 77 to 42% by the presence of 0·2*N*-potassium sulphate.

Measurement of Electrode Potentials.—Although anode-potential measurements were made systematically during the course of the experiments described, it was thought that, owing to the possibility of there being a considerable resistance error with the large currents employed, the results could not be used as evidence. A number of measurements was, therefore, made independently by means of the commutator-extrapolation method (Glasstone, J., 1923, **123**, 2926; 1927, 642); the rate of fall of potential after switching off the current was so great that accurate extrapolation was impossible, but the curves in Figs. 1 and 2 show the general tendencies which were quite marked. More reproducible values were obtained by starting with a high *C.D.* and reducing it in steps than by working in the reverse direction, but the results were of the same type in each case. At low *C.D.*'s and with very small increments of current, breaks were found in the *C.D.*–potential curves, as noted by Shukla and Walker (*Trans. Faraday Soc.*, 1931, **27**, 722). Observations were made in a solution of *N*-potassium acetate and *N*-acetic acid alone, and in one which contained in addition 0·02*M*-manganese, and in a citrate solution of the same p_H (Fig. 1); a 2*N*-acetic acid solution and one to which potassium sulphate was added were also studied, the potential in the latter case being definitely lower than in the former. In Fig. 2 are given the results for 2*N*-potassium acetate solution containing in addition either 0·01*N*-sodium hydroxide or *N*-potassium carbonate, the solutions having p_H *ca.* 12; the potentials in 0·01*N*-sodium hydroxide alone are also included. The *C.D.*–potential curve for *N*-potassium carbonate is almost identical with that for the carbonate–acetate solution. Measurements were made in 2*N*-potassium acetate alone and in the same solution with 0·1*N*-ammonium hydroxide, but the results were so close to those for the electrolyte containing 0·01*N*-sodium hydroxide, especially at the higher *C.D.*'s, that the curves are not included; the potentials in 0·1*N*-ammonium hydroxide solution alone were also very similar to those in the 0·01*N*-sodium hydroxide.

FIG. 1. FIG. 2.



Chemical Oxidation of Acetic Acid and Acetates.—Hydrogen peroxide is known to act on various acetyl compounds with the production of acetyl peroxide (Baeyer and Villiger, *Ber.*, 1900, **33**, 1575), and the controlled decomposition of this substance, under suitable conditions, can give products qualitatively similar to those obtained in the Kolbe reaction (Walker, J., 1928, 2040). According to Schützenberger (*Compt. rend.*, 1865, **61**, 487), barium peroxide, which may be regarded as a substituted hydrogen peroxide, reacts with " l'acide acétique anhydre " to give a gas containing 2 vols. of carbon dioxide to 1 vol. of ethane, *i.e.*, identical with the gas obtained by complete Kolbe synthesis. Attempts to repeat this observation failed (see Glasstone and Hickling, *Chem. and Ind.*, 1934, **53**, 512); in one case a gas having the composition CO_2, 65·9; O_2, 6·1; CO, 1·6; CH_4, 12·0; C_2H_6, 6·1%, was obtained, but this result could not be repeated. By heating concentrated hydrogen peroxide with acetate solutions under various conditions, very small amounts of ethane and methane were sometimes obtained, but the gas consisted mainly of oxygen and a little carbon dioxide.

Gordon (*J. Physical Chem.*, 1914, **18**, 55) investigated the action of persulphates on acetate and obtained some hydrocarbons, but these were mainly either methane or a little ethane accompanied by olefins. A study of his results indicated that ethane was more likely to be obtained by the use of dilute acetate and concentrated persulphate solutions: 30 g. of sodium persulphate (93% $Na_2S_2O_8$) were mixed with 75 c.c. of a 0·1*N*-acetic acid and 0·1*N*-potassium acetate solution in a small flask, and the mixture heated to 85°; the gas evolved was collected and analysed. Experiments were also carried out in the presence of manganese and cobalt salts as catalysts for hydrogen peroxide decomposition; some of the results obtained are given below:

	Analysis of gas, %.						
Catalyst.	CO_2.	O_2.	C_2H_4.	CO.	H_2.	C_2H_6.	CH_4.
None	80·2	0·1	0·4	0·6	0·2	9·8	8·6
0·1*M*-$MnSO_4$	82·5	4·2	0·9	0·7	0·2	2·6	7·8
0·2*M*-$MnSO_4$	52·9	40·6	0·8	0·8	0·5	1·0	1·2
0·5*M*-$CoSO_4$	86·6	8·3	1·3	0·6	0·4	1·3	1·5

In the absence of a catalyst, the products are closely similar to those obtained in the electrosynthesis at low *C.D.*'s. The presence of manganese and cobalt salts inhibits the formation of hydrocarbon in the chemical oxidation and increases the methane/ethane ratio, as in the electrolytic process. It is noteworthy that in the presence of the catalysts the rate of gas evolution was much slower than in their absence, although the gas in some cases contained relatively large amounts of oxygen; this result implies that the behaviour of the catalysts is not due to their action on the persulphate, but on a substance formed from it, presumably hydrogen peroxide, which is the effective agent yielding the hydrocarbons by oxidation of the acetate. If the acetate concentration was increased, the ratio of methane to ethane also increased, a phenomenon also observed in the electrolysis at low *C.D.*'s.

DISCUSSION.

The results of the present work, and those of previous investigators, can be satisfactorily accounted for by supposing, as with other electrolytic oxidations, that hydrogen peroxide is formed by the irreversible union of discharged hydroxyl ions. At high concentrations this is presumably able to oxidise *acetate ions* to ethane and carbon dioxide, $2CH_3\cdot CO_2' + H_2O_2 = C_2H_6 + 2CO_2 + 2OH'$, possibly with the intermediate formation of acetyl peroxide and perhaps the liberation of acetate radicals. The observations on the chemical oxidation of acetic acid and acetates show that this is not improbable, especially when it is remembered that the conditions under which hydrogen peroxide is produced at an anode are very different from those attainable by ordinary chemical means (see J., 1933, 836). Persulphates are hydrolysed in solution to yield hydrogen peroxide, and it is probable that the latter is the effective oxidising agent in the experiments recorded (see above). The effects of the metallic ions in suppressing the Kolbe synthesis are in the order Pb, Ag>Mn>Cu, Co, Fe, and an independent consideration of their catalytic influence on the decomposition of hydrogen peroxide under the conditions prevailing at the anode during the electrolysis of an acetic acid and acetate solution leads to the arrangement of these ions in the groups Pb, Ag, Mn>Cu, Co, Fe. The correspondence of the two series makes it probable that the decomposition of hydrogen peroxide is the factor which determines the suppression of ethane formation, and consequently it is not unreasonable to suppose that the Kolbe reaction depends upon the presence of a high concentration of hydrogen peroxide, formed as an intermediate product.

Further confirmation of this view, and incidentally an explanation of the hitherto incomprehensible behaviour of various electrodes, *e.g.*, gold, in giving no Kolbe synthesis, is obtained from the results of the present study. Smooth platinum and iridium are effective for ethane production (Foerster and Piguet, *loc. cit.*) and both these substances are poor catalysts for hydrogen peroxide decomposition; platinised platinum, however, is a good catalyst, and with an anode of this material there is very little ethane synthesis.

If the electrode is poisoned, by means of mercuric cyanide, potassium cyanide, or sodium fluoride, or better by the addition of a mercuric salt to the platinising solution, the Kolbe reaction can take place, since the peroxide is now no longer decomposed with such great rapidity. Anodic treatment of a platinised platinum electrode decreases its catalytic effect on the decomposition of hydrogen peroxide (Spitalsky and Kagan, *Ber.*, 1926, **59**, 2900) and the corresponding increase in the formation of ethane, first observed but not explained by Foerster and Piguet (*loc. cit.*), has been definitely confirmed. Palladium and iron anodes both dissolve slightly and give almost no ethane (Foerster and Piguet, *loc. cit.*); these substances in true or colloidal solution will undoubtedly be effective in decomposing hydrogen peroxide. The results obtained with the two forms of carbon are in general agreement with the theory, the more finely divided and catalytically active material graphite, which disintegrated considerably during electrolysis, giving the least efficiency for ethane synthesis. Although gold and nickel in the massive form are poor catalysts for hydrogen peroxide decomposition, yet when used as anodes they become covered with oxides which effectively decompose it (p. 1882), and so neither gives the Kolbe synthesis.

The results at low *C.D.*'s or in the presence of catalysts can be accounted for if peracetic acid is supposed to be formed under these conditions. It is well known that this acid results from the action of hydrogen peroxide on acetic acid (*e.g.*, Clover and Richmond, *Amer. Chem. J.*, 1903, **29**, 179; D'Ans and Frey, *Z. anorg. Chem.*, 1913, **84**, 145), and Hatcher and Powell (*Canadian J. Res.*, 1932, **7**, 282) have shown that it is only an oxygen addition product and suggest that it may also be formed by the direct action of oxygen. It is not unreasonable, therefore, to suppose that peracetic acid may be formed by the action of hydrogen peroxide or even by active, perhaps atomic, oxygen on *acetate ions or on acetic acid* whenever the concentration of the peroxide is insufficient to bring about the formation of ethane. The thermal decomposition of peracetic acid gives methyl alcohol and carbon dioxide (see Fichter, *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 131; Fichter and Lindenmaier, *Helv. Chim. Acta*, 1929, **12**, 567), and so the Hofer and Moest reaction, in which methyl alcohol is formed, is to be expected under any conditions which are effective in reducing the hydrogen peroxide concentration while maintaining a supply of active oxygen. The presence of catalysts for the decomposition of hydrogen peroxide should thus result in the replacement of the Kolbe reaction by that of Hofer and Moest, and the experimental results indicate that this is undoubtedly the case. It is significant as further evidence for the intermediate formation of peracetic acid under these conditions that when lead and silver salts are used as catalysts there is considerable oxygen in the gas (Table I); Clover and Richmond (*loc. cit.*) have recorded that lead and silver oxides decompose peracetic acid catalytically with the evolution of oxygen. The possibility that methyl alcohol may be formed by chemical oxidation of acetates is shown by the observation that in certain circumstances this substance can be produced by the action of persulphate on acetate solutions (see Fichter and Lapin, *Helv. Chim. Acta*, 1929, **12**, 998; Fichter and Panizzon, *ibid.*, 1932, **15**, 996).

The action of foreign anions in inhibiting the formation of ethane in the electrolysis of acetic acid solutions was considered by Matsui and Kizaki (*loc. cit.*) to support the discharged-ion mechanism of the Kolbe reaction, it being supposed that the decrease of efficiency was due to preferential discharge of the added anion. In view of the variety of ions able to suppress the formation of ethane (p. 1882), and of the relative effects of such ions as chloride and ferricyanide, this explanation appears highly improbable. The definite parallelism between the mobilities of the anions and their influence on the Kolbe reaction (Table II) suggests an alternative explanation of the observations. In the absence of added anions, acetate ions are continuously brought up to the anode during electrolysis by diffusion, and by electrolytic transport; in addition, the migration of hydrogen ions away from the anode permits of further dissociation of the acetic acid. The amount of acetate ions made so available is sufficient to react with the hydrogen peroxide at the electrode and give a good efficiency, *e.g.*, about 70%, for ethane formation. If, however, a foreign anion is added to the solution, it will compete with the acetate and hydrogen ions, the concentrations of which in acetic acid solution are very small, and will almost completely eliminate transport of current by them. Since very little acetate ion is brought up to the anode in this way, and the accumulation of hydrogen ions tends to suppress the ionisation of the acetic acid, the concentration of acetate ions in the immediate vicinity of the electrode will remain very low. It follows, therefore, that the amount of acetate ion reaching the anode will be dependent mainly on diffusion, and in view of the low concentration in the bulk of the electrolyte this must be small; it can be calculated (cf. Glasstone, *Trans. Amer. Electrochem. Soc.*, 1931, **59**, 277) that in a $2N$-acetic acid solution the acetate ions arriving at the anode in this way would be equivalent to a maximum *C.D.* of 0·0005 amp./sq. cm., it being assumed that the thickness of the diffusion layer in the stirred solution is 0·01 cm., and the diffusion coefficient of the acetate ion 0·74. Since there is an insufficient amount of acetate ion to react with the hydrogen peroxide, the latter will tend to decompose, and the active oxygen so formed, together with some of the peroxide, will react with the acetic acid to form peracetic acid, which then breaks up into methyl alcohol and carbon dioxide. That methyl alcohol is formed when the Kolbe reaction is suppressed by foreign anions is known definitely from the work of Hofer and Moest (*loc. cit.*), from observations made in the course of the present work, and from the number of faradays (n) required to liberate 1 mol. of carbon dioxide, other than that produced by the Kolbe reaction (Table II). The higher the mobility of the added anion the greater should be its effect in reducing the formation of ethane: this is, of course, the experimental fact on which the theory has been developed. If the acetate-ion concentration is increased, the effect of added anions should be less, and this has been verified by experiment; the theoretical change in the discharge potential of the acetate ions, which is logarithmic, would hardly be sufficient to account for the observed differences on the basis of the theory of ionic discharge, but they can readily be explained from the point of view of ionic transport.

The fact that the formation of methyl alcohol occurs in solutions containing bicarbonate is not to be attributed to the alkalinity, but to the presence of the added anions. From the work of Hofer and Moest (*loc. cit.*) it may be seen that, with a smooth platinum anode and a *C.D.* of 0·25 amp./sq. cm. in a solution containing 147 g. of potassium acetate per litre to which 15 g. of potassium hydrogen carbonate have been added, the Kolbe reaction takes place with considerable efficiency, probably about 50%, and this is only reduced to a negligible amount (4—5%) by the addition of about 100 g. of the bicarbonate. This result cannot be accounted for by the difference in p_H of the solutions, which is very small, or by the theoretical decrease of about 0·05 volt in the discharge potential of the bicarbonate ions; a seven-fold increase in concentration of the latter would, however, have a marked effect on the relative amounts of current transported by them and by the acetate ions. Further evidence of the same kind was obtained in the electrolysis of a solution containing $2N$-potassium acetate and $0{\cdot}1N$-ammonium hydroxide made in the present study; the ethane efficiency, at a *C.D.* of 0·25 amp./sq. cm., was initially 52%, but as carbonate accumulated in the electrolyte, providing an alternative ion for the transport of electricity, the efficiency fell off to some extent. It may be concluded, therefore, that the synthesis of methyl alcohol is favoured when the concentrations of either hydrogen peroxide or acetate ions are too small for the Kolbe reaction to occur.

It is now necessary to examine the electrode-potential measurements. The simple view that the formation of ethane in the Kolbe synthesis results from the interaction of two discharged ions occurring above a certain anode potential, *viz.*, 2·14 volt, according to Shukla and Walker (*Trans. Faraday Soc.*, 1931, **27**, 722), meets with a fundamental difficulty which has been overlooked in previous discussions. The potential apparently requisite for the Kolbe reaction is much higher than that required for oxygen evolution at the same *C.D.* in a solution of the same hydrogen-ion concentration not containing acetate (see Figs. 1 and 2). If the anode potential primarily determines the onset of the ethane synthesis, the process should not be appreciable in aqueous solutions, at least until extremely high *C.D.*'s have been attained, but oxygen should be preferentially evolved. A comparison of the *C.D.*–potential curves for solutions of $2N$-potassium acetate containing in one case $0{\cdot}01N$-sodium hydroxide (or $0{\cdot}1N$-ammonium hydroxide) and in the other N-potassium carbonate, both having approximately the same p_H, shows that the potentials in the former solutions, in which the Kolbe synthesis occurs, are much higher than in the latter, where the Hofer–Moest reaction takes place. This fact not only disposes of the view generally held that the formation of methyl alcohol results from the simultaneous discharge of acetate and hydroxyl ions, *viz.*, $CH_3{\cdot}CO_2' + OH' + 2\oplus = CH_3{\cdot}OH + CO_2$, because of the alkalinity of the solution, but it makes it difficult to understand why the Hofer–Moest reaction does not always occur, since it requires a lower potential, in preference to the Kolbe synthesis. It is true that whenever ethane is formed the potential is high, generally greater than 2·14 volt, and when it is inhibited and methyl alcohol results the potential is decreased, but this is no proof that the electrode potential *determines* the process. The potential is to be regarded as determined by the fate of the hydrogen peroxide formed irreversibly at the anode; if this decomposes rapidly, either because of the presence of catalysts or the absence of acetate ions with which to react, oxygen will be liberated at the electrode and the *C.D.*–potential curve is closely similar to that observed for oxygen evolution in a solution of the same p_H not containing acetate ions. If the decomposition of the peroxide is not catalysed and acetate ions are present in sufficient amount, then acetate radicals may be liberated momentarily by the reaction $2CH_3{\cdot}CO_2' + H_2O_2 = 2CH_3{\cdot}CO{\cdot}O{\cdot} + 2OH'$, and since the radicals are more active electromotively than is oxygen, the electrode will acquire a more positive potential, greater than 2·14 volt. The acetate radicals, of course, react very rapidly with one another to yield ethane and carbon dioxide. It is important to emphasise that it is not thermodynamically unsound to postulate that an oxidising agent, *e.g.*, hydrogen peroxide, formed *irreversibly* at a low potential is able to yield by chemical action a product giving a higher, perhaps reversible, potential.

The supposition that electromotively active acetate radicals are formed in this way necessitates, of course, the admission that these radicals can also result from the direct discharge of ions at the same potential. The observations made in the present work, however, lead inevitably to the conclusion that hydrogen peroxide plays an essential part in the Kolbe reaction. The presence in aqueous solution of the more easily discharged hydroxyl ions, which can combine irreversibly to form hydrogen peroxide, results in the direct discharge of acetate ions occurring only to a negligible extent. In non-aqueous solutions, where hydrogen peroxide cannot be formed at the anode, it appears probable that the ethane arises exclusively from acetate radicals discharged directly. The fact that the nature of the anode material has little effect on the Kolbe synthesis in non-aqueous solutions (cf. Fairweather and Walker, *loc. cit.*) would suggest that the mechanism here is fundamentally different from that in aqueous solution; it is hoped to investigate this matter later.

In conclusion, it may be mentioned that the theory of the *primary* formation of acetyl peroxide in the Kolbe reaction (Fichter, *loc. cit.*) might be adapted to account for the experimental observations if it were supposed that the action of the catalysts is to facilitate the decomposition of this peroxide; experimental test has proved, however, that this cannot be the case. A sample of acetyl peroxide was prepared by the method of Gambarjan (*Ber.*, 1909, **42**, 4010), and its solution in anhydrous ether diluted to a concentration of 0·2*N*. To two 20-c.c. portions of this solution was added 0·5 g. of manganese dioxide or of cobaltic oxide; after standing for 3 hours, the solutions were analysed and found to be unchanged. An anhydrous solution of hydrogen peroxide of approximately the same normality, prepared by dissolving " hyperol " in ether, was decomposed vigorously on the addition of either of these oxides.

SUMMARY.

1. The presence of relatively small amounts of lead, silver, manganese, copper, cobalt, and ferrous acetates in a solution of potassium acetate and acetic acid inhibits almost completely the formation of ethane at a platinum anode; the efficiency of the ions is in the order Pb, Ag>Mn>Cu, Co, Fe, whereas their catalytic influence on the decomposition of hydrogen peroxide follows the similar order Pb, Ag, Mn>Cu, Co, Fe. Solid catalysts for the decomposition of hydrogen peroxide also inhibit the Kolbe synthesis, but to a smaller extent.

2. The electrolysis of solutions of sodium, potassium, ammonium, calcium, strontium, barium, magnesium, zinc, nickel, and uranyl acetates gives ethane at the anode in good efficiency; these substances do not catalyse the decomposition of hydrogen peroxide.

3. Although the efficiency of ethane formation is normally very low at a platinised platinum anode, it may be increased if the electrode is prepolarised anodically or suitably poisoned for hydrogen peroxide decomposition by mercuric cyanide, potassium cyanide, sodium fluoride, or mercury. No ethane is obtained in the electrolysis of acetate with gold or nickel anodes; these electrodes become coated with oxides which decompose hydrogen peroxide vigorously.

4. In the absence of added anions, acetic acid gives the Kolbe synthesis, but addition of either potassium fluoride, perchlorate, nitrate, phosphate, chloride, sulphate, or ferricyanide in small concentrations represses this reaction; the effect of these ions runs parallel to their mobilities. Whenever the synthesis of ethane is inhibited and the *C.D.* is not too low, the Hofer–Moest synthesis (formation of methyl alcohol) occurs independently of the alkalinity of the electrolyte.

5. It is shown that the observations made in the present work cannot be accounted for by the theories of the Kolbe reaction hitherto proposed, and an alternative view is suggested, *viz.*, that the irreversible union of discharged hydroxyl ions produces hydrogen peroxide at the anode and this reacts, when in high concentration, with acetate ions to give ethane. If the concentration of the peroxide is kept low, or if there is not available a sufficient concentration of acetate ions, then the formation of methyl alcohol generally occurs, probably through peracetic acid as intermediate stage.

6. The results of the present work indicate that the anode potential is not the primary factor which determines the process occurring in the electrolysis of acetate solutions: it can only be regarded as a secondary indication of the particular reaction taking place.

The authors are grateful to the Royal Society and to the Department of Scientific and Industrial Research for grants.

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[*Received, October* 13*th*, 1934.]