190. *Studies in Electrolytic Oxidation. Part VII. The Electrolysis of Acetates in Non-aqueous Solutions.*

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IN Part VI of this work (J., 1934, 1878) the electrolysis of acetates in aqueous solution was studied, and the conclusion drawn that the anodic evolution of ethane and carbon dioxide (Kolbe reaction) is due to the primary formation, by the irreversible combination of dis-

charged hydroxyl radicals, of hydrogen peroxide, which oxidises the acetate ions, probably with the intermediate production of acetate radicals and possibly acetyl peroxide. The conditions determining the supersession of the Kolbe synthesis by the Hofer–Moest reaction (formation of methyl alcohol) were determined, and it was concluded that this process is an oxidation by oxygen or by hydrogen peroxide of low concentration, and always takes place in aqueous solution when the Kolbe reaction is inhibited. The critical potential (2·14 volts) associated with the Kolbe reaction was regarded as being set up by discharged acetate radicals formed mainly indirectly. It now appeared of importance to investigate the electrolysis of non-aqueous solutions of acetates, since previous work had shown that the Kolbe synthesis can take place in such solutions; as hydroxyl ions are not present, however, the mechanism of the process must presumably be different from that proposed for an aqueous medium. Previous work, of a somewhat sporadic nature, had been carried out with acetic acid and methyl and ethyl alcohols as solvents (Hopfgartner, *Monatsh.*, 1911, **32**, 523; Salauze, *Bull Soc. chim.*, 1925, **37**, 522; *Compt. rend.*, 1925, **180**, 662; Fairweather and Walker, *J.*, 1926, 3111; Shukla and Walker, *Trans. Faraday Soc.*, 1932, **28**, 457; Fichter and Meyer, *Helv. Chim. Acta*, 1933, **16**, 1408; Robertson, *Trans. Faraday Soc.*, 1934, **10**, 1007), but no comprehensive investigation had been made, although the results at elevated temperatures and with various anode materials were sufficient to show that the mechanism of the Kolbe synthesis was fundamentally different from that in aqueous solutions. In the present work, for reasons indicated below, ethylene glycol was used as solvent, and a full study has been made of the influence of all variable factors on the electrolytic process.

<div align="center">EXPERIMENTAL.</div>

In searching for a suitable non-aqueous solvent, the appropriate properties of a number of organic liquids were studied. Acetic acid was rejected since it was not possible effectively to vary the acetate concentration in such a solution, or to work with solutions containing alkali hydroxides, and oxide-coated anodes could not be employed. Methyl and ethyl alcohols were judged unsuitable because of their limited solvent powers, and the difficulty of obtaining them completely anhydrous. Empirical investigation of a large number of organic liquids revealed that ethylene glycol was most suitable : it dissolves most electrolytes giving excellently conducting solutions, and owing to its high b. p. is readily obtained water-free by distillation alone. The glycol employed was purified by fractional distillation, the fraction, b. p. 197—198° (corr.), being used. Acetic acid was purified by the method of Orton and Bradfield (J., 1927, 983); m. p. 16·4°. The potassium acetate used was the commercial " pure " variety; it was powdered, heated in an air-oven at 110—115° for 4 hours, and kept in a vacuum desiccator over calcium chloride. For most of the experiments a stock solution of potassium acetate in the glycol was used; this was boiled for a few minutes previous to use to eliminate traces of water and dissolved gases, and it was then cooled and the requisite amount of acetic acid added.

The electrolytic vessel consisted of a water-jacketed boiling tube (6″ × 1″) fitted with a rubber stopper carrying a thermometer, electrodes, and capillary delivery tube leading to a small mercury trough. The cathode was a piece of stout platinum foil 1 cm. square; the anode was, in general, a spiral of platinum wire of 1 sq. cm. area. Anode and cathode were about 2 cm. apart, and the compartments were not separated unless otherwise stated. Before use, the anode was washed with warm concentrated hydrochloric acid, warm concentrated nitric acid, and water, and heated to redness. Current was supplied from a 40-volt battery through a rheostat and a calibrated milliammeter. 50 C.c. of electrolyte were used in each case. Preliminary electrolysis for 1 hour was found sufficient to saturate the electrolyte with ethane and to displace the air in the apparatus, and was carried out in all cases. In general, about 20-c.c. samples of the mixed anode and cathode gases were collected for analysis in a Bone–Newitt apparatus; carbon dioxide and oxygen were determined by absorption, and ethane and hydrogen by explosion. The sum of the analytical percentages is always close to 100, showing the amounts of other gases present to be negligible. Any methane is, of course, estimated as ethane and hydrogen (since $2CH_4 = C_2H_6 + H_2$), but the work of Shukla and Walker (*loc. cit.*) has shown that appreciable methane formation occurs only at *C.D.*'s lower than any employed in the present investigation. From the ethane/hydrogen ratio the current efficiency for ethane formation was obtained. (Check experiments, measuring the actual volume of ethane formed by the passage of a definite quantity of electricity, showed the method to be satisfactory.) Except where otherwise stated, all electrolyses were carried out at 20°.

3 g

Results.

(In the following experiments, a " stock solution " is one of N-potassium acetate and N-acetic acid in glycol.)

Influence of Duration of Electrolysis.—To determine the effect of duration of electrolysis and to investigate the reproducibility of the results, a stock solution was electrolysed at a *C.D.* of 0·05 amp./sq. cm., samples being collected after 1, 3, and 5 hours' electrolysis. In two sets of experiments the following results were obtained for the efficiency of ethane formation : (1) 69, 66, 65; (2) 66, 66, 63%. It is seen that, if other factors remain constant, duration of electrolysis itself has little influence on the efficiency. The results are in general reproducible to 2—3%.

Influence of C.D.—The influence of *C.D.* was investigated by electrolysing a stock solution with the usual current of 0·05 amp., the size of the anode being varied. The large anodes were of platinum foil and the small ones of platinum wire, all being treated previous to use in the same manner. The following results were obtained :

C.D., amp./sq. cm.	0·5	0·1	0·05	0·01	0·005
Efficiency, %	76	69	66	61	57

The efficiency evidently falls off somewhat with decreasing *C.D.*, although to a less extent than in aqueous solution (see Part VI) ; the relation between efficiency and *C.D.* is an approximately logarithmic one.

Influence of Concentration.—Experiments were made in solutions of varying total acetate concentration at a *C.D.* of 0·05 amp./sq. cm. ; the results were as follows :

KOAc, N	1	0·5	0·25	0·1
HOAc, N	1	0·5	0·25	0·1
Efficiency, %	66	60	56	41

It may be noted that the efficiency falls off with decreasing concentration but not so markedly as in aqueous solution.

Variation of Proportions of Acid and Salt.—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	0·25	0·5	0·75	1·0
HOAc, N	0·75	0·5	0·25	0
Efficiency, %	67	60	56	41

In glycol solution the efficiency falls off somewhat with decreasing acid concentration, although in aqueous solution a maximum efficiency was obtained with an electrolyte consisting of equimolar parts of salt and acid.

Influence of Temperature.—The following results were obtained at a number of temperatures with a stock solution and a *C.D.* of 0·05 amp./sq. cm.

Temperature	20°	40°	60°	80°	98°
Efficiency, %	66	70	69	60	53

It is observed that the efficiency at first rises and then falls with increasing temperature, there being a maximum at about 50°. In aqueous solution the efficiency falls continuously as the temperature is raised, and approximates to zero at 100°.

Influence of Anode Material.—In order to determine the influence of anode material a stock solution was electrolysed with a *C.D.* of 0·05 amp./sq. cm. with various anodes, the apparent area of each anode being 1 sq. cm. Prior to use, the platinised platinum anode was washed with concentrated hydrochloric acid, concentrated nitric acid, water, and acetone, and dried in a current of hot air. The gold anode was washed with concentrated hydrochloric acid, water, acetone, and dried as above. The carbon anodes were washed with water, and then dried after treatment with acetone as above. A nickel anode was tried, but it dissolved in the electrolyte with very little gas evolution. The results are given below.

Anode material	Pt.	Platinised Pt.	Au.	Arc C.	Graphite.
Efficiency, %	66	39	67	71	53

It appears that, if allowance is made for the fact that the actual *C.D.* at platinised platinum and graphite anodes (the latter disintegrated somewhat during electrolysis) is less than at the other anodes, anode material has very little influence on the efficiency, in contrast to its predominating effect in aqueous solution.

Influence of Addition of Water.—Since a gold anode in aqueous solution gives practically no ethane, it was thought of interest to ascertain the effect of small additions of water on the electrolysis in glycol solution. A stock solution was used with a *C.D.* of 0·05 amp./sq. cm. The following results were obtained.

Water, %	0	1	2	3	4	5	10
Efficiency, %	67	56	39	23	10	2	4

It will be noted that the efficiency falls off linearly with the addition of water, reaching the value for aqueous solution at a concentration of water of about 4·7%. To see if the effect of water changes with *C.D.*, experiments were carried out with the usual current of 0·05 amp., but with anodes of different sizes; the results are given below.

C.D., amp./sq. cm.	0·20	0·10	0·05
Efficiency with no water present, %	72	71	67
Efficiency with 4% water present, %	10	13	10

It is seen that within the limits of experimental error a given quantity of water has the same effect in reducing the efficiency independently of *C.D.* It is noteworthy that the addition of water to the glycol solution when a platinum anode is used actually raises the efficiency; *e.g.*, with a solution of *N*-potassium acetate and *N*-acetic acid in glycol and a current of 0·05 amp., the addition of 10% of water raised the efficiency from 66 to 73%.

Influence of Hydroxyl Ions.—To determine whether the water or the hydroxyl ions to which it gives rise are responsible for the inhibition of the synthesis at a gold anode, the effect was studied of adding an alkali hydroxide to the glycol solution. It is impossible to obtain any high concentration of hydroxyl ions, since the carbon dioxide formed at the anode will immediately use up any hydroxide in the vicinity, but it was thought that a small effect might be observed. A solution of *N*-potassium acetate and 0·02*N*-potassium hydroxide in glycol was electrolysed at a *C.D.* of 0·05 amp./sq. cm. with a smooth platinum anode and with a gold anode respectively. The results obtained were :

Anode material	Pt.	Au.
Efficiency, %	40	33

The very small concentration of hydroxyl ions has evidently about the same relative effect on the efficiency of synthesis at a gold anode as has 1% of water. It is probable, therefore, that hydroxyl ions are the effective agents in inhibiting the synthesis when water is added.

Influence of Catalysts for Hydrogen Peroxide Decomposition.—In aqueous solution the addition of small quantities of metallic salts which are catalysts for hydrogen peroxide decomposition inhibits the Kolbe synthesis. It seemed of interest, consequently, to ascertain their effects on electrolysis in the glycol solution. Complications due to the reduction of the metallic salt or deposition of metal at the cathode were avoided by the use of special electrolytic vessels in which the cathode and anode solutions could be separated. These vessels, made by Schott und Gen., of Jena, consisted of flat-bottomed test-tubes (6″ × 1″) divided longitudinally by a porous partition made of fritted glass (porosity G 4) extending to within an inch of the top of the tube. Anode and cathode, mounted in the usual way, were fitted on each side of the diaphragm. These cells were advantageous in that they could be cleaned and dried easily, had very low electrical resistance, diffusion of anolyte and catholyte was negligible, and anode and cathode gases could be collected together in the ordinary way. In all the experiments the catholyte used was 15 c.c. of the stock solution, and the anolyte was 15 c.c. of a solution of potassium acetate and *N*-acetic acid in glycol to which the metallic salt had been added. The catalysts were added as acetates, the solution being made 0·05*M* with respect to the added salt, and the total acetate concentration was *N*. Crystalline lead, manganese, cobalt and copper acetates were dehydrated by heating at 110° for 8 hours, and then kept in a vacuum over concentrated sulphuric acid for several weeks. Ferrous acetate was made directly by dissolving finely divided iron in anhydrous acetic acid. Electrolysis was carried out with the smooth platinum anode at a *C.D.* of 0·05 amp./sq. cm. The preliminary electrolysis was extended to 3 hours to permit complete oxidation of the metallic ions before gas was collected. The following efficiencies were observed :

Catalyst	(None).	Mn.	Pb.	Co.	Cu.	Fe.
Efficiency, %	66	63	66	69	59	64

It is clear that within the limits of experimental error the added substances have no appreciable action in reducing the efficiency, in contrast to their very marked effect in aqueous solution. On the addition of a small amount of water to the glycol solutions, the Kolbe synthesis was largely inhibited; thus the addition of 5% of water to the solutions containing manganese and

copper reduced the efficiencies to 13 and 4% respectively. In view of the observations of Walker and Weiss (*Trans. Faraday Soc.*, 1935, **31**, 1011), it is noteworthy that in neither case was there any visible deposition of oxide on the anode.

Oxide-coated Anodes.—It was thought desirable to ascertain if platinum anodes coated with metallic oxides which are catalysts for hydrogen peroxide decomposition would give the usual ethane efficiency in glycol solution, but difficulty was experienced in obtaining adherent oxide coatings. To help in this connexion, the oxides were deposited on grey platinum, the roughened surfaces serving to retain them, and *N*-potassium acetate in glycol was used as electrolyte; the oxides are less soluble than in the acid solution and the anodic gas evolution is less vigorous since much of the carbon dioxide is retained by the electrolyte. Lead dioxide was deposited by electrolysis of *N*-lead acetate in water at 0·50 amp. for 2 mins. Manganese dioxide was deposited by electrolysis of *N*-manganous acetate in water at 0·05 amp. for 5 mins. An oxide of cobalt could not be deposited. The oxide-coated electrodes were washed thoroughly with water, then with acetone, and dried in an air-oven at 115—120° for 2 hours. The electrolysis was then carried out with an undivided cell and a *C.D.* of 0·05 amp./sq. cm.; the results are given below :

Anode material	Pt.	PbO_2.	MnO_2.
Efficiency, %	41	2	41

It is seen that the manganese dioxide anode gives about the same efficiency as platinum, but the lead dioxide anode gives very little ethane. Observation of the rate of gas evolution at the beginning of the electrolysis seemed to indicate that the lead dioxide anode initially gave a good Kolbe synthesis, but after a time the coating became lighter in colour and the rate of gas evolution decreased, and by the time the preliminary electrolysis was completed very little ethane was being formed. It seems probable that this is a specific action of the lead dioxide (see below).

Potential Measurements.—In order to make measurements of the potentials at which ethane is formed in the glycol solutions, use was made of the commutator-extrapolation method (Glasstone, J., 1923, **123**, 2926; 1927, 642). The anode was provided with the usual Luggin capillary, and this was connected to a calomel electrode with aqueous electrolyte by a bridge containing stock solution, the ends of the syphon being closed by filter-paper plugs. The following values for the anode potential using various electrode materials were obtained at a *C.D.* of 0·032 amp./sq. cm. with *N*-potassium acetate and *N*-acetic acid in glycol as electrolyte; they are expressed on the hydrogen scale in water and all include the same liquid-junction potential.

Anode material	Pt.	Platinised Pt.	Au.	Graphite.	MnO_2.	PbO_2.
Potential, volts	2·16	2·06	2·13	2·13	2·15	1·69

With the exception of the lead dioxide anode, the potentials are approximately the same; the effective *C.D.* at platinised platinum is probably much lower than at the other anodes.

Anodic Oxidation of Glycol.—In none of the electrolytic experiments did the ethane efficiency approach 100%. The gas evolved consisted of ethane with the corresponding amount of carbon dioxide required by the equation for the Kolbe reaction, small but definite amounts of oxygen, usually about 1%, and hydrogen from the cathode. Part of the current must therefore go to oxidise the glycol, and it was found that the electrolytes after each experiment gave a precipitate with 2 : 4-dinitrophenylhydrazine, showing the presence of aldehyde.

Two initial aldehydic oxidation products of glycol are possible, *viz.*, glycollaldehyde and glyoxal. Glycollaldehyde-2 : 4-dinitrophenylhydrazone forms yellow needles, m. p. 155—156° (Collatz and Neuberg, *Biochem. Z.*, 1932, **255**, 29); but we found the m. p. to be greatly affected by minute traces of impurity. An aqueous solution of glycollaldehyde was obtained by hydrolysis of bromoacetaldehyde (Fischer and Landsteiner, *Ber.*, 1892, **25**, 2553) and precipitated with a saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride; the product, after recrystallisation from chloroform–light petroleum, melted fairly sharply at about 137° and gave a correct analysis. Subsequent repeated recrystallisation from 50% methyl alcohol raised the m. p., however, until an ultimate constant value of 158° (corr.) was obtained.

Glyoxal-2 : 4-dinitrophenylhydrazone was obtained as an orange-coloured powder by precipitating an aqueous solution of glyoxal with a saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride. It was only sparingly soluble in most organic solvents and was best recrystallised from nitrobenzene. It then appeared as reddish-orange needles, m. p. 330° (corr.). Decomposition set in a few degrees above the m. p. (Found : C, 39·8; H, 2·4; N, 25·6.* $C_{14}H_{10}O_8N_8$ requires C, 40·2; H, 2·4; N, 26·8%).

* On heating, the substance formed a nitrogenous charcoal which is difficult to burn completely.

To obtain the anodic oxidation products of glycol in quantity, a solution of N-potassium acetate and N-acetic acid in glycol was electrolysed at 0·05 amp. with the smooth platinum anode under the usual conditions for 14 hours. The solution was then diluted, and a saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride added. A yellow precipitate was formed immediately, and after standing for 30 mins., was filtered off and dried; m. p. 140—150°. On recrystallisation from 50% methyl alcohol, it had m. p. 150—152° (corr.). A further recrystallisation gave yellow needles, m. p. 158° (corr.). The oxidation product would therefore appear to be glycollaldehyde. To gain some idea of its amount, a fresh electrolyte solution was electrolysed at 0·05 amp. for 3 hours. The liquid was then diluted, excess of an ice-cold saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride added, and the mixture kept over-night at 0°. The precipitate was then collected in a weighed glass crucible, washed with water, and dried to constant weight at 105—110°. In two experiments the weights of precipitate obtained were 0·102 and 0·106 g., corresponding to a mean value of 16% for the current efficiency of glycollaldehyde formation. As it is unlikely that the hydrazone is completely precipitated, the actual efficiency will probably be greater than this. The ethane efficiency in the electrolysis is 66%, and allowance being made for the small amount of oxygen evolved, it seems evident that glycollaldehyde formation will account for the greater part of the remainder of the current. The result, therefore, seems to leave no doubt that the main product of the anodic oxidation of glycol in the present experiments is glycollaldehyde.

Action of Acetyl Peroxide on Glycol.—For reasons indicated below, the action of acetyl peroxide on glycol was investigated. 1·3 G. of acetyl peroxide dissolved in 15 c.c. of dry ether were added to 20 c.c. of glycol and heated on a water-bath for 30 mins. On testing with potassium iodide, the peroxide was then found to have been completely used up. The liquid was cooled, diluted with water, and excess of an ice-cold saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride added. An immediate yellow precipitate resulted, which was collected and weighed as before, 2·414 g. being obtained, corresponding to a 91% yield of glycollaldehyde calculated on the weight of peroxide taken. The product melted at 152—155° (corr.), and a single recrystallisation from 50% methyl alcohol gave yellow needles, m. p. 158° (corr.).

DISCUSSION.

Since solutions of acetates in glycol have a reasonably good conductivity, and decomposition occurs without the application of excessive voltages, it is evident that acetate ions are readily discharged at the anode, and that the resulting radicals are essentially responsible for the Kolbe reaction which occurs. Apart from this process, however, there are two outstanding observations on the electrolysis of acetate solutions in glycol requiring consideration : these are (*a*) the formation of considerable amounts of glycollaldehyde at any anode, and (*b*) the inhibition of the Kolbe synthesis at a lead dioxide anode. It is highly improbable that oxidation of glycol to glycollaldehyde is a purely electrical process, for, not only is the reaction difficult to formulate, but there is no reason to believe that an alcohol and an aldehyde constitute a definite oxidation–reduction system. It appears, therefore, that chemical oxidation occurs, and in the electrolysis of acetates the effective oxidising agent is probably either the discharged acetate radicals or acetyl peroxide, formed by the combination of these radicals in pairs. The fact that acetyl peroxide reacts readily with glycol, as already described, to give an almost quantitative yield of glycollaldehyde, suggests that the peroxide may well be the active oxidising agent.

This view is supported by the anomalous behaviour of the lead dioxide anode. It was found that on warming lead dioxide for a short time with glycol, oxidation took place and the oxide became yellow; on pouring off the excess glycol and adding a solution of acetyl peroxide in ether, the residue caused vigorous decomposition and evolution of oxygen. The same phenomenon was shown by lead monoxide when mixed with acetyl peroxide in ethereal solution, but the decomposition was only vigorous if a trace of glycol was present. Lead dioxide itself, manganese dioxide, and cobalt sesquioxide did not bring about any decomposition under similar conditions; silver oxide had a slight effect. In electrolysis with the lead dioxide anode, therefore, it would appear that the lead dioxide is slowly reduced by the glycol, and the lead monoxide formed then brings about decomposition of the acetyl peroxide and so inhibits the Kolbe synthesis; this corresponds closely with the experimental observations. The decomposition of acetyl peroxide by lead monoxide is

accompanied by oxygen evolution, but at an anode initially covered with lead dioxide the amount of oxygen in the electrolytic gas is no greater than at other electrodes. In view of the ease with which glycol can be oxidised by nascent oxygen, this result is not surprising. It may be noted, however, that the small amounts of oxygen which are always found in the electrolytic gases may possibly be due to decomposition of the acetyl peroxide.

Since it is necessary to postulate the formation of this peroxide to account for the two observations mentioned above, it is reasonable to assume that all the discharged acetate radicals combine in pairs to give acetyl peroxide. At most anodes, part of it then decomposes to give ethane and carbon dioxide (cf. Walker, J., 1928, 2040; Walker and Wild, J., 1935, 207), and the remainder is utilised in oxidising the glycol. Since acetyl peroxide is hardly affected by any of the anode materials used, apart from lead dioxide after reduction to the monoxide, the Kolbe synthesis in glycol is largely independent of the nature of the anode and of the presence of catalysts for hydrogen peroxide decomposition. On heating, acetyl peroxide tends to decompose into hydrocarbons and carbon dioxide, and hence the electrosynthesis is not greatly affected by rise of temperature, except in so far as the rate of oxidation of the glycol is probably increased. Similarly, other electrolytic factors such as *C.D.* and concentration have only slight effects in non-aqueous solution.
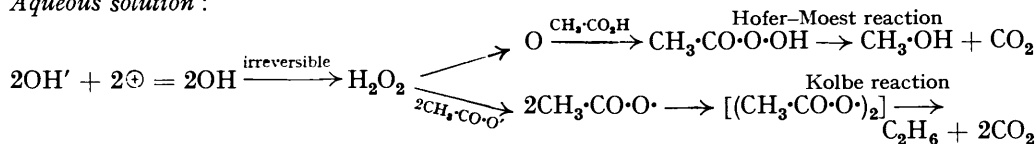
The view that peroxides are intermediates in electrosynthetic reactions with the salts of fatty acids and with the acid-ester salts of dibasic acids has been advocated by Fichter and his collaborators (see Glasstone and Hickling, " Electrolytic Oxidation and Reduction," 1935, pp. 293—295; Fichter *et al., Helv. Chim. Acta*, 1935, **18**, 18, 238, 445, 549, 704, 1005, 1276; 1936, **19**, 149; see also Wieland, Schapiro, and Metzger, *Annalen*, 1934, **513**, 93), mainly as a result of the observed similarity between the electrolytic products and the substances obtained by decomposition of, or chemical interaction with, the appropriate peroxide. In a few instances small amounts of peroxides have actually been detected at the anode by electrolysis under suitable conditions. Fichter, however, has generally held the opinion that the peroxides are not formed from discharged anions, but as a result of chemical oxidation by nascent oxygen. In view of the facts that such oxidation is very improbable in glycol solution, and that the potential at which the Kolbe reaction occurs in this medium is almost constant for a number of different anode materials (p. 822), it is more reasonable to suppose that acetyl peroxide, at least when glycol is the solvent, is formed by the union of discharged acetate radicals. Further, the agreement between the anode potentials in glycol, the liquid-junction being assumed to be small, with that (2·14 volt) required for the Kolbe reaction at a platinum anode in aqueous solution (Shukla and Walker, *Trans. Faraday Soc.*, 1931, **27**, 722; see also Part VI, *loc. cit.*), suggests that if peroxide is formed in the latter solution, as the work of Fichter implies, then it probably arises in this instance also from discharged acetate radicals. The influence of catalysts for hydrogen peroxide decomposition and of neutral salts makes it necessary to suggest, however, that in aqueous solution the radicals are formed mainly as a result of reaction of the acetate ions with hydrogen peroxide, and only to a slight extent by direct discharge at the anode.

On the addition of water or hydroxyl ions to the glycol solutions, hydroxyl-ion discharge will replace that of acetate ions, and if conditions are such as to favour the decomposition of the hydrogen peroxide formed, the Kolbe synthesis will be inhibited. This is seen to be the case in the experiments with the gold anode and in the presence of metallic salts. With small quantities of water the extent to which the synthesis is inhibited will depend upon the amount of water added. When the water present is able to reach the anode at a sufficient rate to provide hydroxyl ions to cope with the whole of the current passing, then direct acetate-ion discharge will no longer occur. As the limiting rate of diffusion of water to the anode under the existing concentration gradient will be very small in the viscous glycol solutions, it is probable that the water is carried to the anode by hydrated acetate ions. This would account for the fact that the influence of a given amount of water is independent of *C.D.*
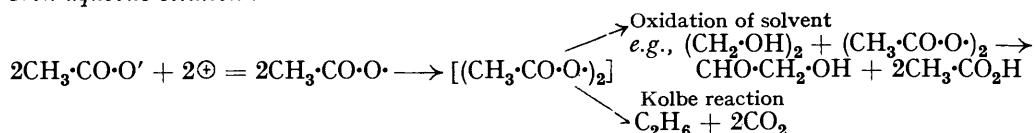
The conclusions reached concerning the electrolysis of acetates in glycol solution would seem to apply equally well to the observations reported with other non-aqueous solutions. Where the solvent is such as not to be readily oxidised, *e.g.*, acetic acid, then the acetyl peroxide is not used up in oxidation reactions and the efficiency for the production of ethane

approximates to 100%. In conjunction with the results of the work in aqueous solution (Part VI) it is possible to present the following comprehensive scheme for the mechanism of the anodic oxidation of acetates.

Aqueous solution :

$$2OH' + 2\oplus = 2OH \xrightarrow{\text{irreversible}} H_2O_2$$

$$O \xrightarrow{CH_3 \cdot CO_2H} CH_3 \cdot CO \cdot O \cdot OH \xrightarrow{\text{Hofer–Moest reaction}} CH_3 \cdot OH + CO_2$$

$$2CH_3 \cdot CO \cdot O \cdot \longrightarrow [(CH_3 \cdot CO \cdot O \cdot)_2] \xrightarrow{\text{Kolbe reaction}} C_2H_6 + 2CO_2$$

Non-aqueous solution :

$$2CH_3 \cdot CO \cdot O' + 2\oplus = 2CH_3 \cdot CO \cdot O \cdot \longrightarrow [(CH_3 \cdot CO \cdot O \cdot)_2]$$

Oxidation of solvent
e.g., $(CH_2 \cdot OH)_2 + (CH_3 \cdot CO \cdot O \cdot)_2 \longrightarrow$
$CHO \cdot CH_2 \cdot OH + 2CH_3 \cdot CO_2H$

Kolbe reaction
$C_2H_6 + 2CO_2$

It must be pointed out that if the first stage of the decomposition of acetyl peroxide in all reactions is the formation of acetate radicals, then the electrolytic results can be explained without the necessity of postulating the intermediate formation of the peroxide, the radicals being the effective agents in both the electrochemical and the chemical processes. At present, it appears impossible to decide between the two interpretations, for even the anodic production of acetyl, or other, peroxide in appreciable amounts would not necessarily be decisive.

SUMMARY.

1. A comprehensive investigation has been made of the electrolysis of acetates in glycol solution with special reference to the Kolbe synthesis : the influence of duration of electrolysis, of *C.D.*, of total acetate concentration, of the ratio of potassium acetate to acetic acid, of temperature, of anode materials (smooth and platinised platinum, gold, arc-carbon, graphite, and manganese and lead dioxides), of small amounts of water, of hydroxyl ions, and of catalysts for the decomposition of hydrogen peroxide, has been studied.

2. The current efficiency for the formation of ethane is generally of the order of 60%, except with a lead dioxide anode, the remainder of the current being mainly devoted to oxidation of the glycol to glycollaldehyde. At an anode initially coated with lead dioxide, which is reduced to the monoxide, the Kolbe efficiency is very low.

3. The anode potentials at which the Kolbe reaction occurs were measured at smooth and platinised platinum, gold, graphite, manganese and lead dioxide anodes : with the exception of the last, the values were almost constant.

4. Acetyl peroxide readily oxidises glycol quantitatively to glycollaldehyde, and the peroxide is rapidly decomposed by lead monoxide, yielding oxygen, especially in the presence of a small amount of glycol. Other oxides, *e.g.*, lead and manganese dioxides, cobalt sesquioxide, and silver oxide, and metals, *e.g.*, platinum and gold, have little action.

5. The results are explained by assuming that acetate ions are discharged at the anode and the resulting radicals combine in pairs to form acetyl peroxide : the latter either decomposes to give ethane and carbon dioxide (Kolbe reaction), or it oxidises the solvent, or it may be decomposed to give oxygen, *e.g.*, by lead monoxide. A scheme for the mechanism of the electrolysis of acetates in aqueous and non-aqueous solutions has been drawn up. It is pointed out that there appears to be no definite means of deciding whether the acetate radical or acetyl peroxide is the effective anodic intermediate.

6. Glyoxal-2 : 4-dinitrophenylhydrazone has been prepared and characterised.

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