

**198. Studies in Electrolytic Oxidation. Part X. The Anodic Oxidation of Acid-Ester Salts: The Mechanism of the Crum-Brown-Walker Synthesis in Aqueous Solution.**

By A. HICKLING and J. V. WESTWOOD.

A complete qualitative and quantitative study of the electrolytic oxidation of potassium ethyl malonate in aqueous solution has been made, and the effect of such variable factors as current density, concentration, acidity, temperature, anode material, presence of foreign cations and anions, and electrode potential on the current efficiency for the formation of ethyl succinate has been investigated. Possible anodic mechanisms are discussed, and it is concluded that none of the views previously advanced will account for the phenomena observed. A new theory, involving the intermediate formation of hydrogen peroxide at the anode, is put forward.

THE fact that electrolysis of a solution of an ester-acid salt of a dibasic acid leads to the production, as main anodic product, of an ester of a dibasic acid containing double the number of  $\text{CH}_2$  groups of the original acid, has been long known (Crum-Brown and Walker, *Annalen*, 1891, **261**, 107; 1893, **274**, 41), and the reaction has frequently been used in the synthesis of long-chain dibasic acids (von Miller and Hofer, *Ber.*, 1895, **28**, 247; Komppa, *ibid.*, 1901, **34**, 900; Bouveault, *Bull. Soc. chim.*, 1903, **29**, 1038; Walker and Walker, *J.*, 1905, **88**, 961; Walker and Wood, *J.*, 1906, **89**, 598; Crichton, *ibid.*, p. 929; Stosius and Wiesler, *Biochem. Z.*, 1920, **108**, 75; Fairweather, *Proc. Roy. Soc. Edin.*, 1925, **45**, 23, 283; 1926, **46**, 71; Fichter and Buess, *Helv. Chim. Acta*, 1935, **18**, 445), but no quantitative investigation of the electrosynthesis seems to have been made even in the simplest case (see, however, Robertson, *J.*, 1925, **127**, 2057, for some electrode-potential measurements), nor has any evidence been adduced in support of the generally accepted view that the synthesis is due to the anodic discharge of the acid-ester ions. The alternative hypothesis, that the reaction is due to a chemical oxidation at the anode, has received some support from the work of Fichter and Lurie (*Helv. Chim. Acta*, 1933, **16**, 885) and Fichter and Heer (*ibid.*, 1935, **18**, 704, 1276; 1936, **19**, 149), who imitated the electrolysis by using potassium persulphate as chemical oxidising agent, and also suggested that organic peroxides may be intermediate products at the anode (Fichter and Buess, *loc. cit.*).

The present investigation was undertaken with a view to making a complete qualitative and quantitative study of the electrosynthesis in the simplest case, *i.e.*, the electrolysis of potassium ethyl malonate to give ethyl succinate, and to deciding whether the chemical or the electrical theory offered the better explanation of the phenomena observed. It was also hoped that some light might be thrown upon the process by the hydrogen peroxide theory of electrolytic oxidation previously developed (Glasstone and Hickling, *J.*, 1932, 2345, 2800; 1933, 829; 1934, 10, 1772, 1878; 1936, 820; Hickling, *J.*, 1936, 1453; Gross and Hickling, *J.*, 1937, 325).

## EXPERIMENTAL.

*Preliminary Investigation.*—In order to determine suitable experimental conditions for exact study, a preliminary qualitative investigation of the reaction was made. Concentrated potassium ethyl malonate solution was electrolysed between platinum electrodes, with an anodic *C.D.* of 0.5 amp./sq. cm., at approximately 0°, a rapid stream of carbon dioxide being bubbled round the cathode to neutralise any alkali formed there. The oil and the aqueous layer were then separated, and examined for esters and acids respectively. On fractional distillation, the oil yielded a little ethyl alcohol, probably resulting from partial hydrolysis of the esters present, and considerable ethyl succinate. A small intermediate fraction, b. p. 120–145°, was also obtained, which gave the characteristic reactions of ethyl glyoxylate. This, therefore, appears to be a product of the electrolysis which has not previously been recorded. The aqueous layer, after being boiled with dilute hydrochloric acid to complete hydrolysis of any esters present, gave strong reactions for succinic and glyoxylic acids (the latter isolated as its 2:4-dinitrophenylhydrazone). The solution also gave an indication of glycollic acid by Denigès's test with sulphuric acid and guaiacol. The gas evolved during the electrolyses was collected over sodium hydroxide and analysed. Apart from carbon dioxide,

it consisted almost entirely of hydrogen (from the cathode), there being only traces of oxygen, ethylene, and carbon monoxide present; saturated hydrocarbons were completely absent. The volume of hydrogen evolved in a given time was very close to the calculated figure, showing that cathodic reduction, if any, was very slight.

*Comprehensive Investigation.*—The following conditions were decided upon for exact study.

In order to avoid the solution becoming alkaline in the vicinity of the cathode, leading to hydrolysis of any esters formed, a solution of potassium ethyl malonate acidified with ethyl hydrogen malonate was used as electrolyte, both substances being supplied by the British Drug Houses Ltd. and being guaranteed free from mineral acids and inorganic salts. The mixture was found to have good buffering properties, and by varying the ratio of salt to acid, solutions of different hydrogen-ion concentration could be obtained; in general, a solution molar with respect to each constituent, and having a  $p_H$  of 3.5, was used (subsequently referred to as the "stock solution").

The electrolytic cell consisted of a water-jacketed boiling-tube (6"  $\times$  1"), fitted with a stopper carrying a thermometer and electrodes. The anode was, in general, a spiral of platinum wire of 1 sq. cm. area, and the cathode was a piece of stout platinum foil 1 cm. square; except where otherwise stated, anode and cathode compartments were not separated. 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 100-volt generator through a rheostat and milliammeter. 20 C.c. of electrolyte were used in each case, and the temperature was kept at 10°, except where otherwise stated, by circulating ice water through the jacket; 0.01 faraday of electricity was passed in all cases, the ethyl succinate formed estimated, and the result expressed as a current efficiency.

After much preliminary work, the following method for the estimation of ethyl succinate was finally adopted. The electrolyte was neutralised with approximately 2N-potassium carbonate, and thoroughly extracted with three 10-c.c. portions of pure benzene. The benzene extracts were then hydrolysed by boiling under reflux for 30 mins. with 25 c.c. of approx. 2N-potassium hydroxide. After hydrolysis, the benzene and alcohol were removed by evaporation under reduced pressure, the solution acidified with nitric acid, approx. 0.5N-potassium permanganate run in dropwise until present in slight excess, and the solution warmed. This removes any glycollic, glyoxylic, malonic, or oxalic acids which may be present. The excess permanganate was removed by addition of a few drops of hydrogen peroxide, the solution neutralised with ammonia, and the succinate precipitated by addition of silver nitrate. To complete the precipitation, the solution (which becomes acid) was again neutralised with ammonia, and absolute alcohol added. The mixture was then filtered through a fine fritted-glass funnel, and the precipitate was washed with aqueous alcohol, dissolved in dilute nitric acid, and estimated by titration with standard ammonium thiocyanate. The method was tested upon electrolyte to which known weights of ethyl succinate had been added. It gave results reproducible to 1–2% but consistently 5% low (this probably represents loss in the extraction). The method was therefore adopted in the investigation, a 5% correction being made in each case. Efficiencies were found in general to be reproducible to 1–2%.

#### Results.

*General Factors.*—The effect of the variation of *C.D.* is shown by the following data obtained for the electrolysis of stock solution :

<i>C.D.</i> , amps./sq. cm. ....	2	1	0.5	0.2	0.1	0.05	0.01
Efficiency, % .....	66	69	74	76	68	48	40

It is seen that there is an optimum *C.D.* of about 0.12 amp./sq. cm., the efficiency falling rapidly as the *C.D.* is decreased.

The results produced by a change of concentration of the electrolyte are illustrated below, the *C.D.* being 0.5 amp./sq. cm. The total amount of malonate present in the electrolysis was kept constant by using appropriate volumes of electrolyte.

$C_3H_2O_4EtK$ , m .....	2	1	0.5	0.25	0.1
$C_3H_2O_4EtH$ , m .....	2	1	0.5	0.25	0.1
Efficiency, % .....	78	74	70	68	30

Hence, ester formation falls off rapidly at low concentrations.

The effect of varying the hydrogen-ion concentration of the electrolyte is shown on the following page, a *C.D.* of 0.5 amp./sq. cm. being used. The  $p_H$  values were measured with the quinhydrone electrode.

The efficiency does not apparently vary much with acidity, but tends to fall off in alkaline solutions.

$C_3H_5O_4EtK$ , M .....	0	0.5	1	1.5	2	2	2
$C_3H_5O_4EtH$ , M .....	2	1.5	1	0.5	0	0	0
						+0.1M-KHCO <sub>3</sub>	+0.1M-K <sub>2</sub> CO <sub>3</sub>
$p_H$ .....	1.4	2.9	3.5	4.8	7.0	8.3	ca. 10
Efficiency, % .....	70	75	74	74	70	64	59

For studying the influence of temperature, the cell was fitted with a reflux condenser, and hot water circulated through the cell jacket. Stock solution was used with a C.D. of 0.5 amp./sq. cm. The results are given below :

Temp. ....	10°	30°	50°	70°	90°
Efficiency, % .....	74	63	56	37	22

The efficiency falls with rising temperature. That this is not due solely to hydrolysis of the ester formed was shown by a blank experiment : 0.5 g. of ethyl succinate was added to 20 c.c. of electrolyte, and the mixture heated to 90° for 30 minutes (period of electrolysis) and then estimated in the usual way. Less than 7% of the ester was found to have been decomposed.

*Influence of Foreign Anions.*—In the electrolysis of acetates, the addition of inorganic salts tends to inhibit ethane formation and leads to the supersession of the Kolbe synthesis by the Hofer-Moest reaction; the effect is particularly marked with acid solutions and is roughly proportional to the mobility of the added anion (Glasstone and Hickling, J., 1934, 1882). To ascertain whether a similar phenomenon would be shown in the present case, 2M-ethyl hydrogen malonate solution was made 0.02N with respect to various potassium salts, and electrolysed at 0.5 amp./sq. cm. with the smooth platinum anode. The results are given below :

*Influence of Foreign Anions.*

Added salt, 0.02N.	(None.)	K <sub>3</sub> Fe(CN) <sub>6</sub> .	K <sub>2</sub> SO <sub>4</sub> .	KCl.	KClO <sub>4</sub> .	KH <sub>2</sub> PO <sub>4</sub> .	KNO <sub>3</sub> .	KF.
Mobility of anion .....	—	97	69	65	64	—	62	47
Efficiency, % .....	70	8	11	19	20	22	23	47

The addition of a weak electrolyte such as boric acid did not decrease the efficiency. In the presence of potassium ethyl malonate the effect of the anions was small unless they were present in considerable concentration; e.g., with stock solution and the C.D. as above, the efficiency of ester formation was reduced from 74 to 38% by the presence of 0.2N-potassium sulphate.

Analysis of the gas from the electrolysis of the ethyl hydrogen malonate containing potassium sulphate showed a current efficiency for oxygen production of approximately 11%. Hence about 78% of the current must go to form some other oxidation product in the solution. To identify this, the electrolysis was repeated, and an acid solution of phenylhydrazine hydrochloride added to the electrolyte. On standing it gave a marked precipitate which, after recrystallisation from benzene, had m. p. 127°; ethyl glyoxylate phenylhydrazone has m. p. 131°. Hence it would appear that when the Crum-Brown-Walker synthesis is inhibited by foreign anions, ethyl glyoxylate is an alternative oxidation product.

*Influence of Nature of Anode Material.*—To determine the effect of the nature of the anode material, experiments were carried out with smooth platinum, grey platinum, platinised platinum (treated in various ways), gold, graphite, gas-carbon (two different samples), nickel, lead dioxide, and manganese dioxide electrodes. The last two electrodes were made by electrodeposition of lead and manganese dioxides respectively on grey platinum. The superficial area of each anode was 1 sq. cm., and stock solution was used with a C.D. of 0.5 amp./sq. cm. Prior to use, the unpoisoned platinised electrodes were cleaned with acid and water as for the smooth platinum anode, the gold and nickel electrodes with warm concentrated hydrochloric acid and water, but in all the other cases water alone was used. The results were as follows :

*Effect of Nature of Anode Material.*

Anode.	Efficiency, %.	Anode.	Efficiency, %.	Notes.
Smooth Pt .....	74	Au .....	12	Anode disintegrated somewhat during electrolysis.
Grey Pt .....	72			
Platinised Pt .....	0	Graphite .....	35	Disintegration in all cases; least with graphite.
Platinised Pt anodically polarised for 4 hours at 0.25 amp. in 2N-NaOH .....	6	Gas-carbon (1) .....	17	
		(2) .....	26	
Platinised Pt poisoned by making platinising solution 0.01M with respect to HgCl <sub>2</sub> .....	10	Ni .....	0	Anode dissolved steadily without gas evolution.
		PbO <sub>2</sub> .....	0	
		MnO <sub>2</sub> .....	35	Oxide tended to strip off during electrolysis.

They are closely similar to those observed in the Kolbe reaction (Glasstone and Hickling, J., 1934, 1881). Platinised platinum normally gives no synthesis, but if its power of decomposing hydrogen peroxide catalytically is decreased, either by anodic polarisation or by poisoning, small yields of the synthetic ester are obtained. Carbon anodes give moderate efficiencies varying with the state of division of the surface. Good catalysts for hydrogen peroxide decomposition, such as gold (which becomes covered with an oxide), lead dioxide, and manganese dioxide, give low efficiencies (the manganese dioxide electrode would probably have given a still lower efficiency if it had been possible to prevent the oxide being stripped off the electrode in the early stages of electrolysis). Analysis of the gas evolved in the above electrolyses showed that, where the efficiency of succinate formation was low, the current was mainly used in oxygen production. Thus the following approximate values of the current efficiency of oxygen formation were observed: lead dioxide anode 91%, platinised platinum 81%, and gold 69%; a little of the current is apparently utilised in other oxidation processes.

*Influence of Catalysts for Hydrogen Peroxide Decomposition.*—To investigate whether catalysts for hydrogen peroxide decomposition would decrease the synthesis efficiency at a smooth platinum anode, as has been found in a number of other cases (Glasstone and Hickling, *loc. cit.*), lead, manganese, copper, cobalt, iron, and silver ions severally, all of which are good catalysts, were introduced into a neutral solution of potassium ethyl malonate, and electrolysis carried out with a *C.D.* of 0.2 amp./sq. cm.; as a control experiment, solutions containing calcium and nickel ions, which are only feebly active, were also used. To avoid introducing foreign anions, the appropriate metallic oxide or carbonate was dissolved in ethyl hydrogen malonate, the solution neutralised with potassium hydroxide, and then diluted to give an anolyte 2M with respect to ethyl malonate ion and 0.01M with respect to the foreign cation. The electrolytic cell was divided by a fritted-glass partition to avoid deposition of metal at the cathode; potassium ethyl malonate solution alone was used as catholyte. The results are given below:

*Effect of Catalysts for Hydrogen Peroxide Decomposition.*

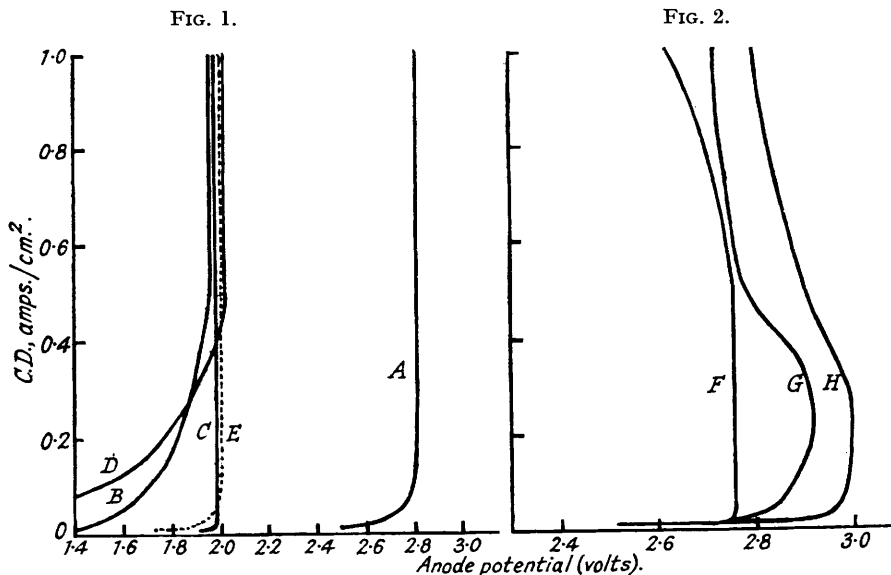
Cation, 0.01M. ....	(None)	Pb <sup>++</sup>	Mn <sup>++</sup>	Cu <sup>++</sup>	Co <sup>++</sup>	Fe <sup>+++</sup>	Ag <sup>+</sup>	Ca <sup>++</sup>	Ni <sup>++</sup>
Efficiency, % .....	78	27	37	38	45	49	50	71	72

Those ions which are good catalysts for hydrogen peroxide decomposition are seen to depress the efficiency of ester formation markedly, whereas those which are feeble catalysts have only a very small effect; the difference between the behaviour of cobalt and nickel is very striking. In acid solution the effects of catalysts for hydrogen peroxide decomposition were less marked although still present; for instance, with the stock solution ( $p_H$  3.5) and other conditions as above, 0.01M-copper decreased the efficiency by 18%, as against 40% for the neutral solution. In the presence of these catalysts for hydrogen peroxide decomposition, the current not used in the Crum-Brown-Walker synthesis appeared to be divided between oxygen evolution and ethyl glyoxylate formation.

*Measurement of Electrode Potentials.*—Some measurements of the anode potentials in the electrolysis of potassium ethyl malonate solutions were made by Robertson (*loc. cit.*), using the direct method, but his results at high currents were almost certainly vitiated by the presence of a large surface resistance error. In the present work, Hickling's electrical interrupter method of measuring polarisation potentials (*Trans. Faraday Soc.*, 1937, 33, 1540) was adopted, and although the rate of fall of potential on interruption of the current was very great (indicating the presence of some extremely unstable electromotively active species), no difficulty was experienced in obtaining reproducible results. In general, the anodes used were 0.1 sq. cm. in area, and they were polarised at 0.05 amp. for some minutes until the potential showed no appreciable drift; observations were then made at a number of different *C.D.*'s. All potentials are expressed on the hydrogen scale. In Fig. 1 are shown the *C.D.*-potential curves for (A) smooth platinum, (B) platinised platinum, (C) gold, and (D) lead dioxide anodes in stock solution; the broken curve (E) is for smooth platinum in a phthalate buffer of  $p_H$  3.5, and indicates what should be the ordinary oxygen evolution potential for the stock solution if no electrolytic oxidation processes took place. In Fig. 2 are shown the *C.D.*-potential curves for the smooth platinum anode in 2M-ethyl hydrogen malonate (F), and in the same electrolyte containing 0.02N-potassium nitrate (G) and -potassium sulphate (H).

A number of interesting features are displayed by the curves. From Fig. 1, it is seen that when the Crum-Brown-Walker synthesis takes place with high efficiency, as at a smooth platinum anode (curve A), the potential, about 2.8 volts, is very considerably higher than the oxygen evolution potential for the same solution, which is about 2.0 volts (curve E). This

indicates unmistakably that the potential associated with this synthesis must be set up indirectly by some process involving an irreversible stage, as otherwise the potential could never be attained, oxygen evolution taking place preferentially. When the synthesis is inhibited by using anodes which are good catalysts for hydrogen peroxide decomposition (curves B, C, and D), the potential drops to the region of oxygen evolution. From Fig. 2, it is seen



that the synthesis in the acid solution takes place at approximately the same potential as for the stock solution, but as the C.D. rises the potential decreases (curve F). This decrease of potential is attended by a diminution in the efficiency of synthesis, as shown by the following figures for the efficiency at a smooth platinum anode in 2M-ethyl hydrogen malonate :

C.D., amp./sq. cm. ....	0.5	1.0	1.5
Efficiency, % .....	70	55	46

In the presence of foreign anions, the initial potential is higher than for the acid alone, but shows the same diminution at higher C.D.'s, the decrease, however, setting in more quickly. The significance of these observations will be considered later.

*Chemical Oxidation of Potassium and Ethyl Hydrogen Malonate.*—By the action of concentrated hydrogen peroxide on the acid ester and its potassium salt under various conditions, small amounts of ethyl glyoxylate were formed, as indicated by the tryptophan test, but no synthesis of ethyl succinate could be definitely established. By using sodium persulphate, which is hydrolysed steadily in solution to give hydrogen peroxide and therefore simulates more nearly conditions at an anode, the electrolysis could be more closely imitated. For instance, on mixing 50 c.c. of stock solution with 51 g. of sodium persulphate (about four times the calculated quantity) and 100 c.c. of water, and heating them on a water-bath for 30 minutes, a 15% yield of ethyl succinate (calculated on the quantity of ethyl malonate ion used) was obtained. Addition of catalysts for hydrogen peroxide decomposition reduced this oxidation efficiency as shown below :

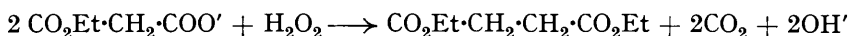
Catalyst.	(None.)	0.1M-MnSO <sub>4</sub> .	0.1M-CoSO <sub>4</sub> .
Yield of ethyl succinate, % .....	15	4	9

Ethyl glyoxylate was also usually formed in the oxidation, particularly in the presence of catalysts for hydrogen peroxide decomposition; e.g., when an oxidation was carried out as above in the presence of manganese sulphate, and a little of the reaction mixture distilled, the distillate had the characteristic smell of ethyl glyoxylate and gave a strong tryptophan test. After hydrolysis, it also gave the Denigès test for glycollic acid, showing this to be one of the products of oxidation.

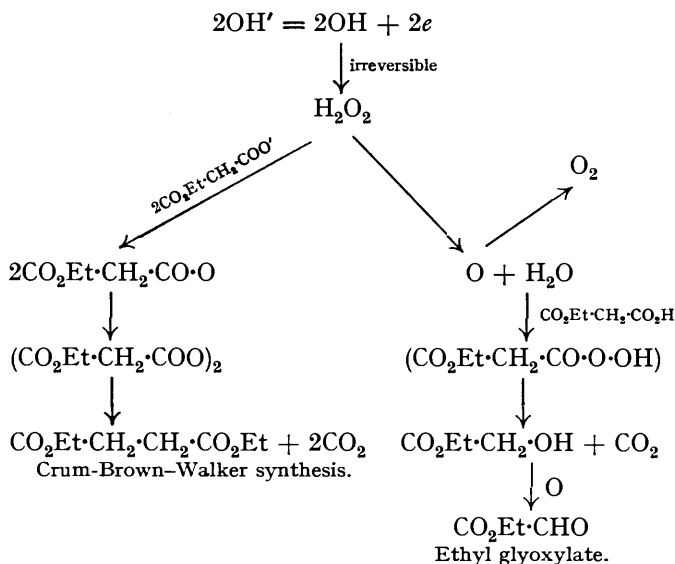
## DISCUSSION.

The phenomena observed in the present work are very similar to those found in the electrolysis of acetates. Two main anodic reactions appear to be possible: (a) the Crum-Brown-Walker synthesis, and (b) the formation of ethyl glyoxylate, probably with ethyl glycollate as an intermediate stage, accompanied by oxygen evolution to a varying extent; reaction (b) appears to predominate when conditions are unfavourable to the Crum-Brown-Walker synthesis. The discharged-ion theory, generally accepted, seems to be inadequate to explain the phenomena observed. For instance, although the effect of *C.D.* and concentration might conceivably be interpreted on this view, it offers no explanation of the influence of temperature, nature of anode material, effect of catalysts for hydrogen peroxide decomposition, and of foreign anions, and it appears quite impossible for the high potential of 2.8 volts, associated with the Crum-Brown-Walker synthesis, to be set up directly in view of the much lower potential of the alternative process. Any theory which attempts to ascribe the oxidation solely to active oxygen at the anode meets similar difficulties.

All the phenomena, however, fall into line if it is postulated that hydrogen peroxide is formed as the primary product at the anode by the irreversible combination of discharged hydroxyl ions. It may be supposed, and in view of the experiments on chemical oxidation seems not unlikely, that when sufficiently concentrated and in the presence of an adequate supply of ethyl malonate ions, the peroxide then reacts to give ethyl succinate:



discharged ethyl malonate radicals and possibly the corresponding acid peroxide being formed as intermediates. If conditions are unfavourable to the stability of hydrogen peroxide, no high concentration of this substance can be formed at the anode, and hence the Crum-Brown-Walker synthesis is inhibited; the hydrogen peroxide of low concentration, and the oxygen arising from its decomposition in the presence of a suitable carrier, may then oxidise the ethyl hydrogen malonate to give the corresponding per-acid, which on loss of carbon dioxide forms ethyl glycollate, this being then further oxidised to the comparatively stable ethyl glyoxylate. The complete scheme is represented below:



It remains now to see how this theory accounts for the phenomena observed, general factors being considered first. At low *C.D.*'s the concentration of hydrogen peroxide at the anode will be low, and hence the rate of ethyl succinate formation will be slow, and much of the hydrogen peroxide will decompose, leading to the alternative oxidation products; this accounts for the falling off in efficiency at low *C.D.*'s. Conversely, high

concentration of ethyl malonate ions will accelerate the ethyl succinate reaction and lead to a high efficiency, thus explaining the effect of concentration. Hydrogen peroxide is much less stable in alkaline than in acid solutions, and hence we should expect the efficiency to decrease as the  $p_H$  of the electrolyte is raised, as is found to be the case; the slight diminution of efficiency in the solution containing acid alone may be attributed to a decrease in the ethyl malonate ion concentration. Rise of temperature increases the rate of hydrogen peroxide decomposition and decreases the efficiency, as would be expected.

The effect of foreign anions in inhibiting the synthesis at a smooth platinum anode in the acid solution may be explained as follows. For formation of ethyl succinate to occur at a reasonable rate, a fairly high concentration of ethyl malonate ions is necessary in the vicinity of the anode to react with the hydrogen peroxide produced there. Some of these ions may arrive at the anode by diffusion from the main body of the solution, but in the acid electrolyte this process will be very slow since the acid is only weakly dissociated and the bulk concentration of ions is low. The majority of the ethyl malonate ions will be brought up to the anode in transporting the current, and at not too high *C.D.*'s will give a concentration sufficient for good synthesis to occur. If, now, an inorganic electrolyte is added, the foreign anion will take over to a considerable extent the transport of current to the anode and therefore interrupt the supply of ethyl malonate ions; the concentration of these ions near the electrode will therefore fall, and hence the efficiency should decrease. The effect should be related to the mobility of the added anion, as is found to be the case. If the view put forward is correct, it would be expected that the effect of added salts should be greatest at high *C.D.*'s, since here ordinary diffusion to the electrode will supply only a negligible fraction of the ethyl malonate ions required. This is borne out by the following figures for 2*M*-ethyl hydrogen malonate with and without potassium sulphate added.

<i>C.D.</i> , amp./sq. cm. ....	0.5	0.2	0.05
Efficiency, % : no added salt .....	70	76	43
"      : 0.02 <i>N</i> -K <sub>2</sub> SO <sub>4</sub> .....	11	42	34
Decrease of efficiency, % .....	59	34	9

In solutions of potassium ethyl malonate it would be expected that the effect of added salts would be less, since the concentration of ethyl malonate ions is much greater than in the acid, and hence ordinary diffusion to the electrode is more marked and the ions can also compete effectively with foreign anions in carrying the current; this is found to be so in practice.

The effect of anode material is readily explicable by the theory of hydrogen peroxide oxidation. Where an anode is a good catalyst for hydrogen peroxide decomposition it would be expected that the efficiency of the Crum-Brown-Walker synthesis would be low. This is found to be the case, platinised platinum, gold, carbon, lead dioxide, and manganese dioxide, all of which are good catalysts, giving low efficiencies. If the activity of the platinised platinum is reduced, either by poisoning or by anodic polarisation, then the efficiency is increased. Addition of metallic salts which are catalysts for hydrogen peroxide decomposition would be expected to reduce the efficiency of ethyl succinate formation at a smooth platinum anode, and this is borne out by the experimental results; of those added, lead and manganese are the most effective catalysts and have the greatest influence on the efficiency. In acid solution the catalytic activity of metallic salts for hydrogen peroxide decomposition is much reduced (probably owing to the difficulty of metallic peroxide formation under these conditions), and they have, correspondingly, less influence on the electrolysis.

If in the reaction of hydrogen peroxide with ethyl malonate ions to give ethyl succinate, discharged ethyl malonate radicals are momentarily liberated, these will be electromotively active and will set up a characteristic static potential against the ethyl malonate ions in solution. The value of this potential will be connected with the concentration of discharged radicals at the electrode surface and the concentration of ions in solution, presumably by an equation of the form

$$\pi = a + b \log_e [\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{COO}]/[\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{COO}' ]$$

where *a* and *b* are constants. Since the anodic formation of hydrogen peroxide involves a

thermodynamically irreversible stage, this potential can be higher than that of alternative electrode processes without any anomaly arising. If, now, conditions are unfavourable to the stability of hydrogen peroxide, decomposition of this to give oxygen and the alternative oxidation products will take place, and the concentration of the discharged ethyl malonate radicals will be very much lowered. Under these conditions, therefore, the potential set up as above may fall below that corresponding to oxygen evolution, and the latter process then determines the observed potential. This agrees exactly with the results displayed in Fig. 1; at low *C.D.*'s a certain amount of oxygen depolarisation may also occur, due to glycollate and glyoxylate formation when the electrode material can function as an oxygen carrier, and the potential will then be somewhat lower (curves *B* and *D*). In the electrolysis of ethyl hydrogen malonate alone, the efficiency falls off at high *C.D.*'s, and this should lead to a decrease in the concentration of discharged ethyl malonate radicals at the anode surface; hence we should expect the potential also to fall, and this rather unusual phenomenon is shown in curve *F* (Fig. 2). When foreign anions are added to the solution, their first effect is to lower the concentration of ethyl malonate ions in the vicinity of the anode, but at low *C.D.*'s the efficiency is not greatly affected, and hence the concentration of discharged ethyl malonate radicals may be supposed to be not greatly diminished. Thus, according to the potential equation, foreign anions at low *C.D.*'s should raise the potential. At higher *C.D.*'s, however, the efficiency is lowered markedly, and hence here we should expect the potential to fall off rapidly. These phenomena are seen in curves *G* and *H*.

The theory advanced thus appears to afford a fairly plausible explanation of most of the phenomena observed in the electrolysis of potassium and hydrogen ethyl malonate solutions in water. In non-aqueous solutions, where hydroxyl ions are not available, it is possible that the mechanism of the synthesis, if it takes place, is different; this point is at present under investigation. The theory should also serve as a guide in the study of the electrolysis of the higher acid ester salts.

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