

242. *Studies in Electrolytic Oxidation. Part XI. The Electrolysis of Acid-Ester Salts in Non-aqueous Solutions, and the Mechanism of the Crum-Brown-Walker Synthesis.*

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A qualitative and quantitative study has been made of the anodic phenomena in the electrolysis of potassium ethyl malonate in ethylene glycol solution. The Crum-Brown-Walker synthesis, *i.e.*, the formation of ethyl succinate, is found to take place with fair efficiency, but is accompanied by marked oxidation of the solvent, mainly to glycollaldehyde. In contrast to the behaviour in aqueous solution, it is found that variable factors, such as temperature, nature of anode material, and presence of foreign cations, have little effect upon the efficiency of ethyl succinate formation. It is concluded that the phenomena can best be explained by supposing that ethyl malonate ions are directly discharged at the anode and the resulting radicals combine to form the acid peroxide; this may then decompose to give ethyl succinate and carbon dioxide, or may alternatively oxidise the solvent, producing glycollaldehyde and generating ethyl hydrogen malonate. A comprehensive scheme for the anodic oxidation of acid-ester salts in both aqueous and non-aqueous solutions is presented.

In Part X of this work (J., 1938, 1039) the electrolysis of potassium ethyl malonate in aqueous solution was studied, and the conclusion drawn that the anodic formation of ethyl succinate and carbon dioxide (Crum-Brown-Walker synthesis) is due to the primary formation, by the irreversible combination of discharged hydroxyl radicals, of hydrogen peroxide, which oxidises the ethyl malonate ions, probably with the intermediate production of ethyl malonate radicals and possibly the corresponding acid peroxide. It was also shown that when conditions are unfavourable to the occurrence of the Crum-Brown-Walker synthesis, an alternative oxidation process leading to the formation of ethyl glyoxylate takes place, and it was concluded that this process is an oxidation by oxygen or hydrogen peroxide of low concentration. The characteristic potential (2.8 volts) associated with the Crum-Brown-Walker synthesis was regarded as being set up by discharged ethyl malonate radicals formed indirectly. It now appeared of importance to ascertain whether the synthesis could take place in non-aqueous solutions where hydroxyl ions are not present, since in this case the mechanism must presumably be different from that proposed for the aqueous medium. No previous work on the occurrence of the synthesis in non-aqueous solutions appears to have been recorded. For reasons indicated below, ethylene glycol was used as the solvent in the present study, and it has been shown that the synthesis can occur with fair efficiency in this medium. A full investigation has been made of the influence of variable factors on the electrolytic process.

EXPERIMENTAL.

Ethylene glycol was selected as the most suitable solvent since it is easily obtained anhydrous and readily dissolves potassium ethyl malonate to give solutions of high electrical conductivity. It was further advantageous in that a complete study of the electrolysis of acetates in glycol had previously been carried out (Glasstone and Hickling, J., 1936, 820), and hence a comparison between the Kolbe and the Crum-Brown-Walker synthesis in non-aqueous solutions could thus readily be made. The glycol employed was purified by fractional distillation, the fraction, b. p. 197—198° (corr.), being used. Potassium ethyl malonate and ethyl hydrogen malonate were specially prepared by The British Drug Houses Ltd., and shown by analysis to be 99.8 and 99.4% pure respectively. Solutions in glycol were made up directly by weight, and, in general, a solution molar with respect both to salt and to acid was used; this is subsequently referred to as the "stock solution."

The electrolytic cell consisted of a water-jacketed boiling-tube (6" × 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

millimeter. 20 C.c. of electrolyte were used in each case, and the temperature was kept at 20°, except where otherwise stated, by circulating ice water through the jacket; 0.01 F. of electricity was passed in all cases, the ethyl succinate formed estimated, and the result expressed as a current efficiency.

For the estimation of the ethyl succinate, the method of analysis described in Part X (J., 1938, 1039) was used, the electrolyte being first diluted with water. The glycol, owing probably to its very small solubility in benzene, did not interfere in any way, and check experiments with known amounts of ethyl succinate gave results reproducible to 1—2%.

Results.

Preliminary Investigation.—To determine whether the electrosynthesis of ethyl succinate does take place in glycol solution, three 20-c.c. portions of the stock solution were each electrolysed at 0.5 amp. for 90 mins. The electrolytes were mixed, diluted with water, neutralised with potassium carbonate, and extracted with ether. The ethereal extract was dried over calcium chloride and then distilled. A considerable quantity of ester having the characteristic odour of ethyl succinate, b. p. 215°, was obtained, which on hydrolysis gave succinic acid, m. p. 184°.

To ascertain whether any oxidation of the glycol takes place during electrolysis, the residue from the ethereal extraction was treated with 2:4-dinitrophenylhydrazine hydrochloride solution, and the resulting yellow precipitate, recrystallised from methyl alcohol, melted sharply at 159°, undepressed on admixture with the same derivative, m. p. 159°, prepared from glycollaldehyde specially synthesised (Collatz and Neuberg, *Biochem. Z.*, 1932, 255, 29).

The gas evolved during an electrolysis under standard conditions was collected over mercury and completely analysed in a Bone-Newitt apparatus: it consisted almost entirely of carbon dioxide and hydrogen (from the cathode), with a small amount, less than 1%, of oxygen; hydrocarbons were not present. 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.

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

<i>C.D.</i> , amp./sq. cm.	0.5	0.2	0.1	0.05	0.01
Efficiency, %	57	54	52	51	46

It is seen that, although the efficiency is in general rather less than for aqueous solutions, yet it does not fall off so rapidly with decreasing *C.D.* (see Part X).

The results produced by a change of concentration of the electrolyte are illustrated below, the *C.D.* being 0.2 amp./sq. cm. The total amount of malonate present in the electrolysis was kept constant by using appropriate volumes of electrolyte.

$C_2H_3O_4EtK$, M	1	0.5	0.25	0.1
$C_2H_3O_4EtH$, M	1	0.5	0.25	0.1
Efficiency, %	54	52	45	37

The efficiency falls off with decreasing concentration but not so markedly as in aqueous solution.

The effect of varying the proportions of potassium ethyl malonate and ethyl hydrogen malonate while the total malonate ion concentration is kept constant is shown below, a *C.D.* of 0.2 amp./sq. cm. being used.

$C_2H_3O_4EtK$, M	0.5	1	1.5	1.75	2
$C_2H_3O_4EtH$, M	1.5	1	0.5	0.25	0
Efficiency, %	56	54	41	28	20

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

The following results were obtained at a number of temperatures with a stock solution and a *C.D.* of 0.2 amp./sq. cm. :

Temperature	20°	40°	60°	80°	100°
Efficiency, %	54	56	46	41	38

The efficiency at first rises and then falls slowly with increasing temperature; in aqueous solution it falls rapidly and continuously as the temperature is raised.

Influence of Anode Material.—In order to determine the influence of anode material a stock solution was electrolysed with a *C.D.* of 0.2 amp./sq. cm. with various anodes, the apparent area of each anode being 1 sq. cm. Prior to use, a 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, and acetone, and dried as above. The carbon anodes were washed with water, and then dried after treatment with acetone as above. The results are given below :

Anode material	Pt	Platinised Pt	Au	Arc C	Graphite
Efficiency, %	54	39	57	55	46

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 platinised platinum anode in aqueous solution gives practically no ethyl succinate, 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 0.2 amp./sq. cm., and the following results were obtained :

Water, %	0	1	2	3	4	5	6	7	10
Efficiency, %	39	35	29	26	21	18	15	12	2

Within the limits of experimental error, the efficiency falls off approximately linearly with the addition of water.

The influence of water is apparently independent of *C.D.* as is shown by the following results :

<i>C.D.</i> , amp./sq. cm.	0.2	0.1	0.05
Efficiency with no water, %	39	37	37
Efficiency with 5% water present, % ...	18	16	19

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 Crum-Brown-Walker synthesis. It seemed of interest, consequently, to ascertain their effects on electrolysis in the glycol solution. To avoid reduction of the metallic salt or deposition of metal at the cathode, a cell divided by a fritted-glass partition was used. To obviate the introduction of foreign anions, the ethyl malonate derivative of each metal was prepared by the action of potassium or hydrogen ethyl malonate on the metallic acetate or carbonate, respectively. The salts thus prepared were dried for some hours at 115°, the metal present estimated, and then a solution of the salt in stock solution made up so as to contain 0.01 g.-atom of metal per litre. The solutions were electrolysed with a *C.D.* of 0.1 amp./sq. cm. The results are given below :

Catalyst	(None)	Mn	Pb	Co	Cu	Ag
Efficiency, %	54	52	49	48	50	49

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.

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 efficiency in glycol solution. Some difficulty was experienced in obtaining adherent oxide coatings which would not dissolve in the acid solution, but the roughened surface of grey platinum was found to retain them, and 2M-potassium ethyl malonate 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 0.5 amp. for 3 mins. Manganese dioxide was deposited by electrolysis of N-manganous sulphate in water at 0.05 amp. for 5 mins. The oxide-coated electrodes were washed thoroughly with water, then with acetone, and dried in an air oven at 110° for 1 hour. The electrolysis was then carried out with an undivided cell and a *C.D.* of 0.2 amp./sq. cm. The following results were obtained :

Anode material	Pt	PbO ₂	MnO ₂
Efficiency, %	20	6	20

It is seen that the manganese dioxide anode gives the same efficiency as platinum, but the lead dioxide anode gives only a small amount of synthesis.

Potential Measurements.—Measurement of the anode potentials in glycol solution by the direct method was found to give completely misleading results owing to the presence of a very large surface resistance error which could amount to several volts even at comparatively low currents. Use was therefore made of Hickling's electrical interrupter method (*Trans. Faraday Soc.*, 1937, 33, 1540), and reasonably reproducible results were easily obtained. 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 of the anode potentials were then made at a *C.D.* of 0.2 amp./sq. cm., which was that usually employed in the synthetical experiments. Except for the measurements with the oxide-coated anodes, in which 2M-potassium ethyl malonate was used as electrolyte, stock solution was used throughout. The potentials observed are given below; they are expressed on the hydrogen scale in water and all include the same liquid-junction potential.

Anode material	Pt	Au	Platinised Pt	C	MnO ₂	PbO ₂
Potential, volts	3.41	3.33	3.21	3.42	3.45	2.21

With the exception of the lead dioxide anode, the potentials are approximately the same, but rather higher than the value of 2.8 volts found for the synthesis in aqueous solution. The *C.D.*-potential curves have not yet been explored in detail, but preliminary observations indicate a number of peculiar features, in particular a falling off of potential at high *C.D.*'s.

Anodic Oxidation of Glycol.—In none of the electrolytic experiments did the efficiency of the Crum-Brown-Walker synthesis approach 100%, and hence part of the current must go to oxidise the glycol. The preliminary experiments had already shown that a certain amount of glycolaldehyde was formed during electrolysis. To gain some idea of its amount, stock solution was electrolysed with a smooth platinum anode and a *C.D.* of 0.2 amp./sq. cm. for the usual time, the electrolyte diluted, and excess of an ice-cold saturated solution of 2 : 4-dinitrophenylhydrazine hydrochloride added. After standing overnight at 0°, the precipitate was collected in a weighed glass crucible, washed with water, and dried to constant weight at 105–110°. 0.256 G. of precipitate was obtained, corresponding to a current efficiency for glycolaldehyde formation of 22%. As it is unlikely that the hydrazone is completely precipitated, the actual efficiency will probably be somewhat greater than this. The efficiency of the Crum-Brown-Walker synthesis in the same experiment was 54%. Hence rather less than 24% of the current is unaccounted for by the two above processes. Some of this will be taken up in bringing about the small amount of oxygen evolution which was observed, and the remainder may be accounted for by further disintegrative oxidation of the solvent, of a nature not yet established, since the gas analysis showed rather more carbon dioxide to be present than would be expected from the Crum-Brown-Walker synthesis alone.

Bis(carbethoxyacetyl) Peroxide, CO₂Et·CH₂·CO·O·O·CO·CH₂·CO₂Et.—For reasons indicated below, it was decided to attempt the preparation of this peroxide. The peroxides of this series have not received much attention, although Fichter and Buess (*Helv. Chim. Acta*, 1935, 18, 445) prepared the adipic analogue and showed that on thermal decomposition it gave products similar to those obtained in the electrolysis of potassium ethyl adipate. The acid chloride was therefore prepared by the action of thionyl chloride on ethyl hydrogen malonate (Marguery, *Bull. Soc. chim.*, 1905, 33, 546) and purified by vacuum distillation. 15 G. of the chloride were then dissolved in 50 c.c. of ether and cooled to – 10° and a paste of 17 g. of hydrated barium peroxide in 50 c.c. of ether at the same temperature added. The mixture was shaken for 2 hours at – 10°. It was then filtered, the filtrate dried over anhydrous sodium sulphate, and evaporated in a vacuum at room temperature. About 5 g. of a viscous oil of slight but characteristic odour were obtained. This substance reacted slowly with potassium iodide and permanganate, and gave a slight coloration with titanous sulphate which deepened rapidly. Hence it appeared that the crude organic peroxide, probably contaminated with hydrogen peroxide, had been obtained. It was used for the following experiments without purification.

Thermal decomposition. A small quantity of the peroxide was heated in a flask over a small flame. Quiet decomposition took place, and a residue boiling at 214–218° and having the odour of ethyl succinate was obtained. The experiment was repeated with 1.003 g. of crude peroxide, the ethyl succinate formed being determined in the usual way; a yield of 27% calculated on the weight of crude peroxide taken was obtained.

Action on glycol. 0.9 G. of the crude peroxide, dissolved in 10 c.c. of ether, was added to 20 c.c. of glycol, and the mixture warmed slowly to 100° on a water-bath; it was then diluted

with water and excess of a solution of 2 : 4-dinitrophenylhydrazine hydrochloride added. After standing overnight at 0°, the precipitate was collected in a glass crucible, dried at 105—110°, and weighed; 0.131 g. was obtained, corresponding to a 16% yield of glycollaldehyde, calculated on the weight of crude peroxide taken.

DISCUSSION.

The results now obtained are exactly parallel to those observed in the electrolysis of acetates in glycol solution (Glasstone and Hickling, *loc. cit.*), and it would seem that a similar explanation would apply to the two cases. It may be supposed that ethyl malonate ions are directly discharged at the anode to form ethyl malonate radicals which then combine to give the corresponding peroxide; this may then decompose to give ethyl succinate and carbon dioxide, or may react with the solvent forming glycollaldehyde as the initial oxidation product. The experiments on the thermal decomposition of the prepared peroxide, and its reaction with glycol, support this view.

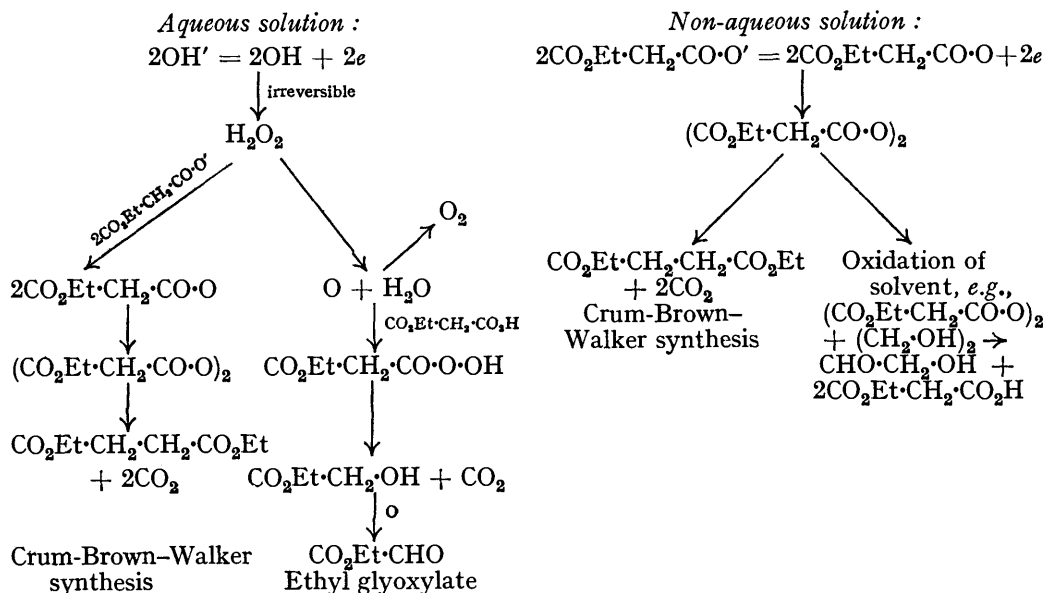
Since the ethyl malonate ions are *directly* discharged at the anode, in contrast to the process suggested for aqueous solutions in which it is supposed that hydrogen peroxide is the primary anodic product and that this then reacts with the ions, it would be expected that variable factors should have little influence on the electrolysis except in so far as they may effect the stability of the organic peroxide or its reaction with the glycol. This is in agreement with the experimental observations. As has already been pointed out, the synthesis in glycol solution is practically independent of the nature of the anode material or of the presence of catalysts for hydrogen peroxide decomposition, both of which factors are of predominating importance in aqueous solution. The falling off in efficiency at a lead peroxide anode in glycol solutions, which was also observed in the case of acetates, is probably to be attributed to reduction of the lead peroxide to monoxide by the glycol, the basic monoxide then reacting chemically with the organic peroxide to form a lead salt with evolution of oxygen; the organic peroxide may then act upon the solution of the lead salt, re-forming lead peroxide, and the process may repeat itself indefinitely. This view was confirmed experimentally in the case of acetates; it has not been found possible to do so in the present instance, as it is very difficult to obtain the organic peroxide free from hydrogen peroxide, and the reaction of the latter with the lead oxides masks the effect being sought.

The falling off in efficiency of the Crum-Brown-Walker synthesis in glycol with decreasing acid concentration is of some interest. Although no certain explanation is yet available, it seems not improbable that the organic peroxide is most stable in the presence of excess acid, and that some process akin to hydrolysis takes place when the acid concentration is diminished. The influence of temperature on the synthesis is much what might be expected. On heating, the organic peroxide tends to decompose into ethyl succinate 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.

On the addition of water to the glycol solutions, hydroxyl-ion discharge will replace that of ethyl malonate ions, and if conditions are such as to favour the decomposition of the hydrogen peroxide produced, the Crum-Brown-Walker synthesis will be inhibited. This is seen to be the case in the experiments with the platinised platinum anode. 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 discharge of ethyl malonate ions 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 ethyl malonate ions. This would account for the fact that the influence of a given amount of water is apparently independent of *C.D.*

In conjunction with the results of the work in aqueous solution (Part X) it is now possible

to present the following comprehensive scheme for the mechanism of the anodic oxidation of the acid-ester salt in aqueous and in non-aqueous solutions.



The authors gratefully acknowledge grants from the British Association for the Advancement of Science (to J. V. W.) and the Chemical Society.

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[Received, June 1st, 1939.]