CCLXXXI.—*Anode Phenomena in the Electrolysis of Potassium Ethyl Malonate.*

By JOHN BRAITHWAITE ROBERTSON.

R. E. GIBSON (this vol., p. 475) has shown that the synthesis of trichloromethyl trichloroacetate by electrolysis of trichloroacetic acid takes place only when the anode potential exceeds 2·34—2·37 volts on the hydrogen standard and concluded that the anode process is one of direct oxidation. However, as he points out, this is not a carbon to carbon synthesis, and it appeared desirable to determine whether similar results would be obtained in a true Kolbe synthesis.

As in the apparatus devised for measuring anode potentials, only small currents could be employed, and therefore only small quantities of synthetic product obtained, potassium ethyl malonate proved to be a very suitable material because, whereas this salt is very soluble in water, the diethyl succinate formed on synthesis is an oil and sparingly soluble in the solution employed. On production of this oil a change in the appearance of the gas bubbles leaving the anode was easily observable, as Gibson found to be the case with trichloroacetate. When no synthesis occurred, these were small in size and left the anode freely, but as soon as the oil was formed they became much larger and appeared to cling to the anode, a phenomenon attributable to their being coated with a thin film of the synthetic oil.

Preliminary experiments showed that a change occurred at a potential of about $\epsilon_H = 2{\cdot}3$, where ϵ_H is potential referred to the normal hydrogen electrode as standard. Below this potential .the gas evolved at the anode was chiefly oxygen, whereas above this potential scarcely any oxygen was produced, the gas being almost pure carbon dioxide.

A series of determinations was carried out to fix this point more exactly. Measurements were made at different values of the applied *E.M.F.* between the electrodes of (1) the anode potential, (2) the current, and (3) the volume and composition of the gases evolved in unit time. Similar measurements were also made when electrodes of (1) platinised platinum, (2) grey platinum, and (3) gold were used. The apparatus employed is practically identical with that described by Gibson, except that here it was not necessary to have the anode and the cathode in separate compartments.

The potential difference between the anode and a calomel electrode was measured by the compensation method, with use of an Ostwald decade rheostat, a battery of accumulators, a sensitive galvanometer, and a standard cadmium cell. The current passing through the electrolyte was measured on a milliamperemeter, and the *E.M.F.* between the electrodes on a shunted voltmeter.

After all necessary connexions had been made, the current was switched on and the voltage adjusted to give the desired *E.M.F.* between the electrodes. Readings of the anode potential were made at intervals. The potential took a considerable time to become constant, in general about an hour, but in some cases several hours; with gold electrodes within a certain range no steady reading was obtained even after a constant *E.M.F.* had been applied for 12 hours. When equilibrium was reached, the evolved gases were collected for a measured length of time varying from $\frac{1}{2}$ hour to 3 hours (depending on the current passing) until at least 20 c.c. were obtained. During this time frequent regular readings of anode potential and current were made, and the means of these were taken as representing the potential and current during the period. If these readings varied by more than a few hundredths of a volt or a few milliamperes, as the case might be, the experiment was abandoned. The amount of hydrogen found on analysis served as a check on the amperemeter readings. It was necessary to determine only the carbon dioxide and oxygen in the gas sample, the residue being hydrogen. Several tests with fuming sulphuric acid showed that no unsaturated hydrocarbon gases were produced.

The results are detailed on p. 2060 : *c* is the current in milliamperes, ϵ_H the anode potential, and CO_2 and O_2 are the volumes (c.c at *N.T.P.*) evolved per hour.

The solution used in each case was *N*-potassium ethyl malonate. The values for carbon dioxide do not represent the total carbon dioxide produced, as a considerable proportion of this remains in the solution, being fixed as carbonate or bicarbonate by the alkali formed round the cathode, but they are useful for purposes of comparison.

The diagrams show curves for oxygen evolved per hour and current carried plotted from the above data, the numbers of the diagrams corresponding with those of the tables on p. 2060.

With smooth platinum electrodes (IB) there is, between anode potentials of 2·30 and 2·37, a sudden drop in oxygen evolved. A similar drop, although not so sharp, occurs with grey platinum electrodes (IG) at a potential of about 2·4. The characteristic change in the nature of the bubbles leaving the anodes was also apparent about these points. This value of 2·3—2·4 therefore corresponds to the potential at which the synthesis of diethyl succinate occurs. A large-scale experiment with grey platinum electrodes and a current of 1 ampere showed that above this potential synthesis took place as with smooth platinum, a film of oil appearing on the surface of the electrolyte after about 15 minutes. This value of the anode potential is the same as that found by Gibson (*loc. cit.*) in the formation of trichloromethyl trichloroacetate. The shape of the current curve, however, differs from his. Whereas he found a drop in the curves on formation of the ester, here a fairly sharp rise takes place. In order to determine whether the difference was due to the different natures of the reactions or simply to differences in apparatus and working conditions, Gibson's experiment was repeated using the apparatus already described but replacing the platinum foil anode by one of platinum wire. With *N*-trichloroacetic acid, a similar curve to Gibson's was obtained.

IB.

Electrodes : Two pieces of bright platinum foil, each 20 × 25 mm., 1 cm. apart.

c.	ϵ_H.	CO_2.	O_2.
20	2·02	0·7	2·3
24	2·12	0·7	3·0
31	2·16	1·5	4·1
37	2·27	1·7	5·3
44	2·30	2·1	6·2
63	2·37	4·0	2·6
88	2·39	7·0	2·5
123	2·45	20·6	0·5

IG.

Electrodes : Grey platinum. Two pieces of foil, 10 × 10 mm., which had been platinised, then gently ignited in a spirit lamp flame, 1·5 cm. apart.

c.	ϵ_H.	CO_2.	O_2.
36	2·28	0·4	6·1
42	2·31	0·6	6·6
54	2·35	1·5	7·8
73	2·40	2·3	8·2
84	2·44	3·5	7·3
105	2·49	4·4	7·6
181	2·6—2·7	9·2	5·8

II.

Electrodes : Platinised platinum wire, 2 cm. long and 0·5 mm. in diameter, 1·5 cm. apart.

c.	ϵ_H.	CO_2.	O_2.
24	2·24	0·1	5·0
31	2·29	0·1	6·0
38	2·32	0·1	7·5
53	2·43	0·1	10·1
65	2·53	0·3	12·9
91	2·68	0·4	17·1
103	2·77	0·7	19·3
121	2·88	1·1	22·3
135	3·00	1·5	24·7
142	3·10	1·9	25·6
168	3·25	3·7	29·2
185	3·33	7·0	29·1
202	3·50	19·7	21·9
210	3·78	18·4	14·5

III.

Electrodes : Gold wires, 1 mm. in diameter, 1 cm. apart. In the first six experiments these were 2·5 cm. long. The length was then reduced to 0·5 cm. With a similar anode potential the current carried was then exactly 1/6th of that given with the larger electrodes. The actual results obtained for current and gases evolved in the first six experiments have been divided by 6 to make the whole series comparable.*

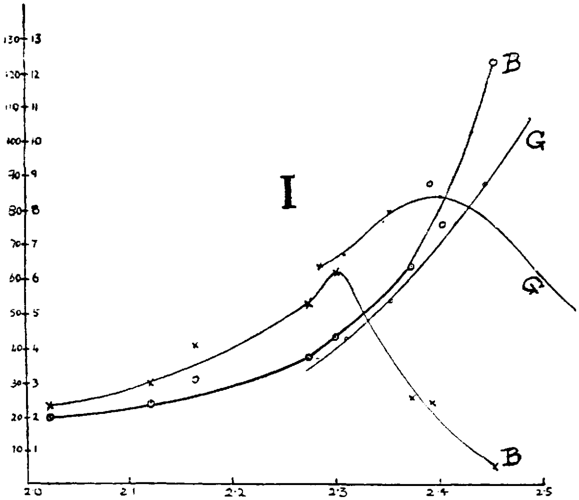
c.	ϵ_H.	CO_2.	O_2.
4·3	2·28	0·05	0·8
7·0	2·52	0·07	1·4
10·5	2·77	0·1	2·0
14·0	2·88	0·1	2·7
20	3·12	0·2	3·7
24	3·28	0·2	4·7
30	3·57	0·2	6·1
32	4·24	0·2	6·2
32	4·43	0·3	6·5
35	5·01	0·3	6·8
111	6·22	1·0	21·4
133	6·31	1·3	24·9
158	6·52	1·8	30·9
240	6·76	2·2	44·9

This type of curve was also given when potassium trichloroacetate was used as electrolyte. With potassium ethyl malonate, however, a curve similar in all respects to that of Fig. 1 was obtained. The difference is therefore connected with the nature of the reactions at the anode and may be conditioned by the presence or

* The gold electrodes even under low potentials soon became coated with a brown covering of dispersed gold. The current and potential readings, however, were quite as constant as in the case of platinum, so it may be assumed that in spite of this "spattering" the surface area remained practically constant throughout.

absence of halogen. Gibson assumes that the anode changes from "platinum α," which is stable at low potentials and which does not favour synthesis, to "platinum β," stable above 2·2 volts and favouring synthesis. The following facts would seem to lend support to this view. After a solution of potassium ethyl malonate had been electrolysed for a time at an anode potential above the synthetic value the applied *E.M.F.* was reduced so as to bring the anode potential below this value; the resulting current always approximated after a short interval to that obtained when ascending the curve. This was not the case when potassium trichloroacetate was the electrolyte. For instance, a solution of the latter was electrolysed for 20 hours at a high potential. The anode potential was then 2·8 volts and the current 0·3 m.a. The applied *E.M.F.* was then reduced, the anode potential becoming 2·2 volts and the current 0·07 m.a. On the ascending curves the current corresponding to this potential was 0·65 m.a., nearly ten times as large. The anode was still covered with the large bubbles typical of synthesis, although the potential was now well below the synthetic potential. On removing these bubbles by rubbing with a piece of wire (without interruption of the current), although there was a momentary rise of current, it subsequently returned

FIG. 1.



Curve IB : *Bright platinum.* *Curve* IG : *Grey platinum.*

Horizontal axis : anode potential, ϵ_H, in volts.

Vertical axis : on left, current in milliamperes ⊙ *; on right, oxygen per hour in c.c.* ×.

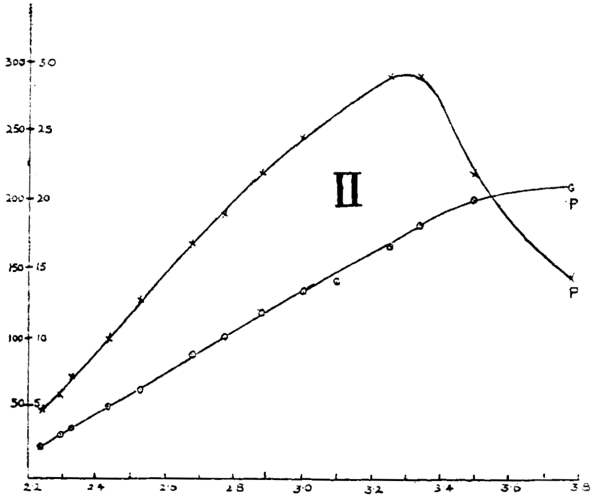
rapidly to 0·07 m.a. as large bubbles reformed on the anode. Repeated rubbings effected no permanent change. The electrolysis was then allowed to proceed undisturbed for 5 days with the same constant applied *E.M.F.* At the end of this time, anode potential was still 2·2 volts, but the current had increased to 0·7 m.a., a value agreeing well with the 0·65 m.a. obtained in the ascending series. On Gibson's hypothesis, these results are simply explained by assuming that "platinum β" was formed on the surface of the anode during its period of high potential, that this "platinum β" continued to function as a synthetic agent on reduction of the potential below the normal synthetic value, but after the lapse of sufficient time it, being metastable at low potentials, had gradually reverted to "platinum α" with resulting cessation of synthesis and rise of current.

Interpretation of the Results.—When potassium ethyl malonate is electrolysed, the anion $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}O'$ is discharged at the anode. On discharge, this may react with the water, or with another similar anion, or the oxygen liberated from the water may oxidise ethyl hydrogen malonate. These possibilities are shown in the equations, where R stands for $CH_2{\cdot}CO_2Et$.

$$\begin{aligned}
&\text{Ia.}\quad 2R{\cdot}CO{\cdot}O + H_2O = 2R{\cdot}CO_2H + O.\\
&\text{Ib.}\quad 2R{\cdot}CO_2H + O = R{\cdot}R + 2CO_2 + H_2O.\\
&\text{II.}\quad 2R{\cdot}CO{\cdot}O = R{\cdot}R + 2CO_2.\\
&\text{III.}\quad R{\cdot}CO_2H + 10\ O = 5CO_2 + 4H_2O.
\end{aligned}$$

Other subsidiary reactions may occur, but in the case of the malonates these are very limited in degree. Equation Ia represents the reaction of the anion with water with liberation of atomic oxygen. If this atomic oxygen unites with another atom, molecular oxygen is produced and escapes as gas at the anode. An equivalent quantity of hydrogen will be produced at the cathode by the reaction of the potassium ions, and the whole therefore amounts to the simple electrolysis of water. Equation Ib represents the formation of diethyl succinate as a result of the oxidation of the ethyl hydrogen malonate formed at the anode by the atomic oxygen simultaneously liberated. Equation II represents two discharged anions as uniting to form the same product, a molecule of carbon dioxide splitting off from each of them. Equation III represents complete oxidation of hydrogen ethyl malonate to carbon dioxide and water. It remains to determine which reactions prevail with the different electrodes and with different potentials. In general, equation Ia represents the prevailing reaction at low potentials. It would appear justifiable to look on this reaction as being maintained during rise of potential and to consider reaction Ib, II, or III as being superimposed on it (compare Gibson, *loc. cit.*, p. 482).

FIG. 2.



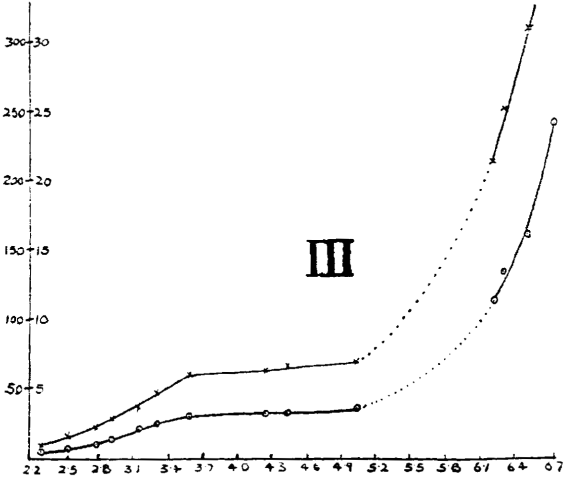


FIG. 3.

Curve II : *Platinised platinum.* *Curve* III : *Gold.*

Horizontal axis : anode potential, ϵ_H, *in volts.*

Vertical axis : on left, current in milliamperes ⊙ ; *on right, oxygen per hour in c.c.* ×.

There are then three possible forms of oxygen curve. (1) If reaction Ia alone holds throughout the whole range, the amount of oxygen evolved per unit time would be directly proportional to the current, and would rise steadily with increasing potential, giving a continuously ascending curve. (2) If reaction II were superimposed at any stage, since no oxygen is either used up or produced by it, presumably the oxygen curve would here reach a maximum and then remain approximately at that value. (3) If either reaction Ib or III was superimposed, some of the oxygen formed in reaction Ia would be used for oxidation work and a fall in the value of oxygen evolved per unit time would thereby result.

We will now apply this reasoning in turn to each of the cases studied.

Bright Platinum (Curve IB).—The oxygen curve rises with increase of potential and current to a maximum at a potential of 2·3 and then rapidly falls until at potential = 2·45 practically no oxygen is evolved. Synthesis of diethyl succinate therefore takes place at anode potential = 2·3, and this synthesis is performed with the help of the atomic oxygen liberated at the anode or according to equation Ib. This point is therefore an oxidation potential, not a discharging or decomposition potential, as it would be if equation II held. It will be noted also that the current curve begins to rise steeply about this point, although no break has been shown in the curve. This can be readily explained as being due to depolarisation of the anode resulting from the oxygen removal. At low potentials, the oxygen is never equal to half the hydrogen, as it would be if reaction Ia occurred alone, an appreciable quantity of carbon dioxide being always produced. This may result from either reaction Ib or III taking place, *i.e.*, either synthesis occurring below the apparently limiting potential or complete oxidation of part of the electrolyte. It is probable, as will be shown later, that the oxygen deficiency represents a complete oxidation of a small portion of the electrolyte to carbon dioxide and water (compare Murray, *loc. cit.*).

Grey Platinum (Curve IG).—The curves for grey platinum resemble those for smooth platinum, the maximum in the oxygen curve being, however, less sharp. It is also noteworthy that before this point is reached the carbon dioxide evolved became relatively high as with smooth platinum. The reactions taking place are therefore probably the same in both cases. Although there is no direct experimental evidence to support the hypothesis, it seems probable that the comparative differences may be due to differences in surface current density.

Platinised Platinum (Curve II).—The oxygen and current curves rise steadily until an anode potential of about 3·3 is reached. The oxygen curve then falls while the current curve still ascends, although somewhat less steeply. If any synthesis takes place, it is exceedingly small in amount, as is proved by the fact that on electrolysing 100 c.c. of solution between platinised platinum electrodes for 2 hours with a current of 2·5 amperes and extracting the resulting solution with ether, there remained on removal of the ether only a trace of an oily film which had not the characteristic odour of diethyl succinate. It would appear, therefore, that above an anode potential of 3·3 complete oxidation of the electrolyte (equation III) takes place in amount sufficient to produce a fall in the oxygen evolved. This is also shown by the larger increase in carbon dioxide. Below this value, only small quantities of carbon dioxide are produced, and relatively these are very much smaller compared with the oxygen evolved than is the case with smooth platinum. In order to test conclusively whether carbon dioxide is evolved at very low potentials, the following experiment was carried out. A modified apparatus was used which allowed a current of air free from carbon dioxide to be passed through the electrolyte. This was fitted with platinised electrodes and half filled with malonate solution to which a few drops of dilute sulphuric acid had been added. With no current passing, a slow stream of air was aspirated through the solution and then bubbled through a single drop of lime water contained in a small bubbling apparatus. After 2 hours there was no sign of milkiness in the lime water. This proved the malonate solution to be free from carbonate. A current of 10 milliamperes was then passed with an anode potential of 1·83, the same air current being continued. After ¼ hour there was evidence of carbon dioxide and after 1 hour the milkiness was very definite. Oxidation was therefore taking place even at this very low potential. Since there is little doubt that the only oxidation occurring with platinised platinum is the complete oxidation of equation III, this would support the conclusion that in the case of smooth platinum the carbon dioxide produced at low potentials is due to this reaction.

Gold (Curve III).—With gold electrodes at low potentials there is a very small yield of carbon dioxide, but its presence was proved by an experiment similar to that described in the case of platinised platinum. It probably represents a small amount of complete oxidation. The oxygen evolved rises steadily till a potential of 3·6 is reached, then remains practically constant till potential = 5·0. Thereafter occurs a region of oscillating potentials. With an applied *E.M.F.* between the electrodes of 7·3 volts, the current varied during 12 hours between the limits of 40 and 8 milliamps., with corresponding anode potential variation of 5·0—6·0. Both rise and fall were very slow, each occupying from 1 to 2 hours, and they showed no diminution in magnitude with time. Above potential = 6·2, rapidly ascending smooth curves are obtained. The carbon dioxide evolved remains very small throughout and even at the highest potential reached the oxygen deficiency is only about 10%. It would thus appear that with gold there is very little oxidation of any kind, the main reaction throughout being that of equation Ia. The peculiar nature of the curves between anode potentials of 3·6 and 6·2 is doubtless due to some form of electrode effect, most probably the formation of an oxide of gold. On this assumption one can imagine that at potential 3·6 the atomic oxygen liberated at the anode, instead of combining to form molecular oxygen, begins to combine with the gold. This tendency continues until potential = 5·0, the gradual reduction in conductivity of the electrode due to the formation of the film of oxide rendering this portion of the curve flat. Above this potential, *i.e.*, throughout the dotted portion of the curve where readings were not obtainable, the oxide film is alternately formed and destroyed as the potential varies between about 5·0 and 6·0, the lower potential favouring the formation of oxide and the higher one causing it to decompose with oxidation of the electrolyte. The variation in the conductivity of the electrode during these changes accounts for the changes in current, which throughout shows oscillations in an inverse direction to those of the potential. The final sharp rise in the curves represents a range where the oxide is either not formed or is destroyed as soon as formed and no polarising effect occurs.

Summary.

(1) The formation of diethyl succinate on electrolysis of potassium ethyl malonate is shown to be an oxidation reaction and to take place only when the anode is of a suitable material and when its potential exceeds 2·3—2·4 volts referred to the normal hydrogen electrode as standard. The results are in general agreement with the views expressed by Gibson.

(2) Grey platinum resembles smooth platinum in its behaviour as electrode material.

(3) With platinised platinum and with gold anodes no synthesis occurs; but whereas the former at a potential of 3·3 causes a large oxidation of the electrolyte to carbon dioxide and water, with the latter little oxidation occurs even at potentials over 6.

(4) What appears to be complete oxidation of a portion of the electrolyte occurs with all the anode materials used, even at very low potentials. The extent of this oxidation is small with platinised platinum and gold, more considerable with smooth platinum and grey platinum.

(5) With gold a peculiar instability is observed, and an explanation of this is suggested.

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