THE ELECTROLYTIC FORMATION OF SODIUM PERBORATE. Part I.

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Sodium perborate is readily obtained when a saturated solution of borax containing an equivalent quantity of sodium hydroxide is treated with an excess of hydrogen peroxide⁽¹⁾:

$$Na_2B_4O_7 + 2\,NaOH + 4\,H_2O_2 = 4\,NaBO_3 + 5\,H_2O\,.$$

S. M. Tanatar⁽²⁾ states that perborates are produced at the anode by the electrolysis of concentrated solutions of sodium orthoborate, but E. J. Constam and J. C. Bennette⁽³⁾ could not confirm Tanatar's results.

Sodium perborate is an industrial product and is manufactured chemically as well as electrochemically. In the electrochemical process the presence of sodium carbonate is necessarily requisite for the production of perborate, while it is not so in the chemical one. Accordingly two distinct views have been proposed as to the significance of the presence of sodium carbonate in the electrolytic formation of perborate; one counting the carbonate as nothing essential to do with the anodic reaction, and the other considering that it plays a part therein.

Tanatar⁽⁴⁾ assumes that borate is oxidised by hydrogen peroxide formed at the anode, and K. Arndt⁽⁵⁾ consideres that the active oxygen produced at the anode as a result of OH-ion discharge is responsible for perborate formation. Both of these investigators are alike representatives of the former view. F. Foerster,⁽⁶⁾ on the other hand, states that percarbonate is primarily produced at the anode, and the hydrogen peroxide which results from the hydrolysis of the former is responsible for the oxidation in question. The present author is inclined to consider, according to the results of following experiments, that the electrolytic formation of perborate is rendered possible only through the intermediate production of percarbonate.

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(1) S. M. Tanatar, *Z. physik. Chem.*, **26** (1898), 132; *ibid.*, **29** (1899), 162; B. Bruhat and H. Dubois, *Compt. rend.*, **140** (1905), 506.

(2) *Loc. cit.*

(3) *Z. anorg. Chem.*, **25** (1900), 265.

(4) *Loc. cit.*

(5) *Z. Elektrochem.*, **28** (1922) 263.

(6) "Elektrochemie wässeriger Lösungen," 4th Ed. (1923).

In addition to the study of the mechanism of the anodic reaction a comparison of electrolysis using diaphragm with that without it is made, as well as a study of the effects of adding several foreign substances from a practical point of view.

Experimental and Discussion.

For the purpose of electrolyses with diaphragm a spiral of Pt-wire of 0.5 mm. diameter is used as the anode, rotating at the centre of a porous cylinder which, standing at the centre of a beaker, makes the anode chamber. The anode is thoroughly ignited immediately before electrolysis. The cathode is also a spiral of Pt-wire placed against the inner wall of the beaker. The anolyte which is 120 c.c. at the commencement of electrolysis and suffers litte decrease in volume at the end of it is kept at 15°C. by cold water circulating through a spiral of glass tubing immersed in the cylinder, and is stirred at the same time by the rotation of the anode. The catholyte is N-sodium hydroxide solution in all cases. The same amount of electricity, 1020 coulombs, is supplied in each electrolysis, unless otherwise mentioned.

For the purpose of electrolyses without diaphragm the same anode is employed as above, rotating at the centre of the electrolytic vessel, a stout test-tube, which is surrounded by cold water to keep the anolyte at 15°C. The cathode is a Pt-wire spirally wound against the wall of the vessel. In these cases also, the same amount of electricity, 1020 coulombs, is supplied, unless otherwise mentioned. The electrolyte which is 100 c.c. at the beginning, in this case, is not less than 99.5 c.c. at the end of electrolysis.

The analysis of the electrolyte is performed as follows: When there is no solid in the electrolysed solution, which is the case in most instances, duplicate portions of 30.0 c.c. are treated with sulphuric acid and subsequently titrated with N/10 potassium permanganate. When there is a considerable amount of solid in the solution, the latter together with the former is treated, as a whole, in the way mentioned above. It is assumed that the peroxidic product which reacts with permanganate is sodium percarbonate when the original solution contains merely sodium carbonate, but sodium perborate when the solution contains borate.

Electrolyses with Diaphragm. Three solutions are electrolysed as anolyte to see the effect of current density on the current efficiency which is varied 5–50 amp./dm.^{2} Table 1 and Fig. 1 show the results.

Table 1.

Solution \ Current density (amp./dm.^{2})	5	10	20	30	40	50
(1) 0.5 mol Na_2CO_3+0.1 mol $Na_2B_4O_7$ per liter	30.7	37.2	42.5	46.7	47.3	47.8
(2) 1.0 mol ,, +0.1 mol ,, ,, ,,	38.1	43.8	49.8	52.4	51.9	52.7
(3) 1.5 mols ,, +0.1 mol ,, ,, ,,	41.1	47.9	54.5	56.1	58.6	59.3

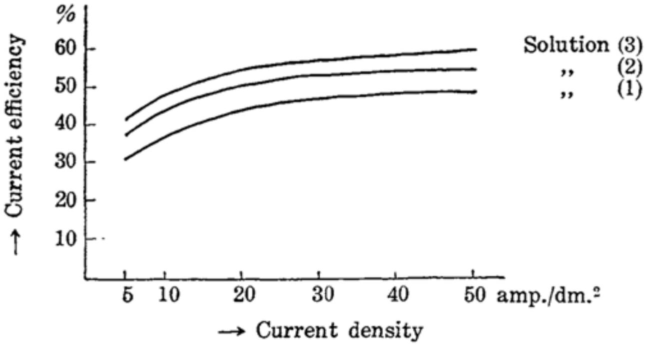

Fig. 1.

As illustrated in Table 1 and Fig. 1, the increase of sodium carbonate concentration in these cases is favourable to the current efficiency of perborate production. Increase of current density is also favourable to the same and its effect is more remarkable when the current density is comparatively smaller than when it is greater.

Perborate, as can be seen from following experiments, is hardly formed by the electrolysis of borate by itself and sodium carbonate is, at least from the practical point of view, indispensable for its electrolytic production. According to P. C. Alsgaard(7) an addition of sodium carbonate causes some decrease in the solubility of perborate, yet sodium carbonate is not likely to affect the present electrolyses in this respect, since crystallisation of perborate does not take place in any of above experiments. The fact, however, that the increase of sodium carbonate increases the current efficiency seems to be in favour of the view that carbonate plays some part or other in the present electrochemical reaction.

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(7) *Trans. Am. Electrochem. Soc.*, **40** (1921), 139.

Change of Current Efficiency with Time. The four solutions are electrolysed, as anolyte, with the current density of 10 amp./dm.^{2}, the results of which are shown in Table 2.

Table 2.

Time (min.) Solution	15	30	45	60	90
(2) see Table 1	67.7	61.9	57.8	51.3	46.4
(3) ,,	68.6	66.4	61.8	53.3	50.1
(4) 1.0 mol Na_2CO_3 solution saturated with borax	69.3	60.9	56.0	55.7	43.0
(4) 1.0 mol Na_2CO_3 solution only	56.5	51.7	41.7	37.5	28.2

Current efficiency steadily decreases with time in each case. Although the total content of perborate or percarbonate in the respective solution increases with time, the current efficiency decreases. That is to say that the rate of the increase of the peroxidic product is decreasing.

Electrolyses of Metaborate Solutions. In order to examine the possibility of perborate formation from metaborate the solutions shown in Table 3, as anolyte, are electrolysed.

Table 3.

Current density (amp./dm.^{2}) Solution	5	10	20	40
(6) 0.4 mol sodium metaborate per liter	2 drops	1	0.5	0
(7) 0.8 mol ,, ,,	3	6	3	1
(8) 1.2 mols ,, ,,	3	7	3	—
(9) 0.4 mol metaborate + 0.8 mol NaOH per liter	—	0	0	—
(10) 0.4 mol metaborate + 0.8 mol KOH ,,	0	0	0	—

Numbers of drops in Table 3 refer to titers of N/10 potassium permanganate for 30.0 c.c. portions of electrolysed anolytes, and a rough idea of current efficiency can be obtained from the following example, viz., 7 drops of permanganate solution correspond to 1.2% current efficiency. When the anolyte contains free alkali besides metaborate in these experiments, no peroxidic product is formed at all, but it is formed, although in a small amount, when the anolyte consists of metaborate only.

As it seems interesting to the author to make out the reason why the production of the peroxidic compound is so scanty, if any in these cases—either because it is immediately decomposed after its formation, or because its production is initially small—the following experiments are made.

Rate of Decomposition of Peroxidic Compounds. Solutions (2), (5), and (7), after being electrolysed as anolyte with the current density of 20 amp./dm.^{2} (0.566 amp., half an hour), are examined as to their content of peroxidic oxygen; a 25.0 c.c. portion of each solution is titrated with N/10 permanganate after standing for the under-mentioned period (Table 4).

Table 4.

Temp. (°C.)	Time (min.) / Solution	0	15	30	45	60	90	120
50	(2)	12.5 c.c.	—	8.05	—	5.85	—	3.90
	(5)	6.50	—	1.50	—	0.70	0.40	0.30
	(7)	3 drops	3 drops	3 drops	—	—	—	—
80	(2)	12.6 c.c.	2.75	1.65	0.60	0.45	—	—
	(5)	6.1	0.75	0.35	0.10	—	0	—

Assuming that the peroxidic compound contained in Solution (2) is perborate and that contained in Solution (5) percarbonate, it is clear from the above expriments that the former peroxidic compound is much more stable than the latter. Although the electrolytic formation of perborate from borate by itself is hardly possible from the practical point of view, it will be so if percarbonate which is easily producible by electrolysis and, at the same time, is liable to decompose can be transformed, by some process or other, into perborate which is more stable than the former. And above facts show that such is likely to be the mechanism by which perborate is electrolytically produced in the presence of carbonate.

Stability of perborate in metaborate and carbonate solutions is now examined. Solutions containing 0.8 mol metaborate and 1.0 mol sodium carbonate per liter respectively are saturated with sodium perborate crystals and then treated in the same way as in the previous experiment. The results are shown in Table 5, where numbers of c.c. refer to the titres of N/10 permanganate.

Table 5.

	Time (min.) / Temp. (°C.)	0	15	30	60	90
Solution (7) sat. with perborate	50	15.0 c.c.	13.4	12.1	9.1	9.1
Solution (5) sat. with perborate	50 80	15.0 14.8	13.5	8.3 0	3.6	2.2

Further, an electrolysis of Solution (7) saturated with perborate is undertaken to see to what extent perborate is decomposed during electrolysis. The current density is 20 amp./dm.^{2} (0.566 amp., half an hour) and the N/10 permanganate titres of 25.0 c.c. portions of the original solution, the one immediately after above electrolysis, and the original solution after standing for half an hour at the same temperature as in the electrolysis, i.e., 15°C., are 15.0, 9.1, and 14.9 c.c. respectively. These results show that the decomposition of perborate during electrolysis is not to such an extent as exhausting. Conditions under which perborate exists in these cases may not be quite identical with those of electrolyses of metaborate solutions, still it is evident from above facts that perborate is much more stable in the metaborate solution than in the carbonate one. It is probable, therefore, that the small current efficiencies as regard to perborate production in electrolyses of metaborate solutions are due to its initial production itself being minute, but not to the fact that perborate which is once formed in a greater amount is mostly decomposed in subsequent instances.

Electrolyses without Diaphragm. The following solutions are electrolysed for the purpose of observing the effects of disusing diaphragm and also of adding foreign substances :

(11) 0.5 mol Na_2CO_3 + 0.1 mol $Na_2B_4O_7$ + 1.0 g. K_2CrO_4 per liter,
(12) 1.0 mol ,, + 0.1 mol ,, + 1.0 g. ,, ,, ,
(13) 1.5 mols ,, + 0.1 mol ,, + 1.0 g. ,, ,, ,
(14) 1.0 mol ,, + 30 g. ,, + 0.1 g. ,, ,, ,
(15) 1.0 mol ,, + 30 g. ,, + 0 g. ,, ,, ,
(16) 1.0 mol ,, + 30 g. ,, + 0.1 g. K_2SO_4 ,, ,
(17) 1.0 mol ,, + 30 g. ,, + 0.5 g. ,, ,, ,
(18) 1.0 mol ,, + 30 g. ,, + 0.1 g. KCl ,, .

Their current efficiencies are shown in Table 6, and some of them represented graphically in Fig. 2. Current densities are varied just as in the case of electrolyses with diaphragm, the amount of electricity supplied being the same, 1020 coulombs, in all cases.

Current efficiency is increased by the increase of current density for the same amount of electricity. Solutions (11), (12), and (13), which respectively differ from Solutions (1), (2), and (3) which are electrolysed with diaphragm in containing 1.0 g. K_2CrO_4 in addition per liter, are inferior to the latter three with respect to current efficiency.

Table 6.

Current density (amp./dm.^{2}) / Solution	5	10	20	30	40	50
(11)	9.6%	19.6	23.2	26.0	25.5	23.7
(12)	19.6	27.8	34.3	37.1	36.4	39.6
(13)	21.4	29.8	36.4	39.2	41.0	41.7
(14)	30.3	42.1	51.4	54.4	59.6	57.2
(15)	30.1	38.9	49.3	51.4	55.6	56.0
(16)	30.0	39.2	47.8	50.3	53.9	54.9
(17)	23.2	34.6	45.3	49.9	52.4	52.8
(18)	27.8	40.7	48.5	52.8	55.3	58.5

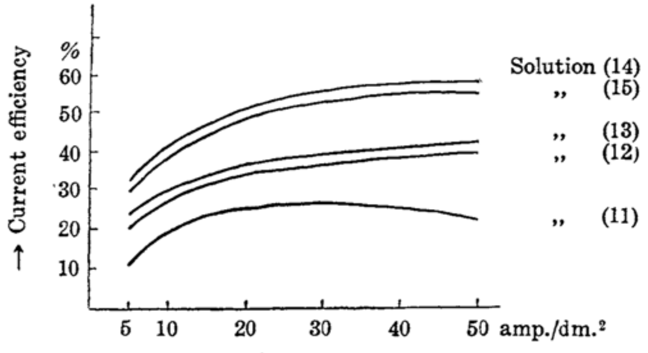

Fig. 2.

Potassium chromate consumes part of the peroxidic oxygen when the solution is treated with sulphuric acid for the sake of titration. And when it is contained as much as 1.0 g. per liter in the solution, its negative effect on current efficiency is probably more than compensated by the positive one which may have occurred during the course of electrolysis. When potassium chromate is contained in a very small amount, e.g. 0.1 g. per liter as in Solution (14), its presence is so advantageous that the current efficiency is decidedly greater than that of any of Solutions (11), (12), and (13) and is nearly equal to that of Solution (3) in spite of its smaller content of borax.

It is rather striking that the current efficiency of Solution (15) which contains no foreign substance is equal to those of Solutions (2) and (14), because the presence of potassium chromate in the electrolyte was generally considered to be advantageous to perborate production. Solutions containing sulphate tend to decrease their current efficiencies and this tendency is the greater, the more sulphate is contained. This is because the persulphate which is produced at the anode side by side with perborate decreases the apparent current efficiency, being incapable of reacting with permanganate. The presence of sulphate in a small amount is not specially favourable. Solution (18) containing 0.1 g. of potassium chloride gives a good current efficiency, yet there is an unavoidable disadvantage, in this case, that the Pt-anode is attacked by its presence.

Change of Current Efficiency with Time at Constant Current Density. Solution (15) which contains sodium carbonate and borax but no other foreign substance is electrolysed with the current density of 20 amp./dm.^{2} The current efficiency, as shown in Table 7, gradually decreases as time goes on to 120 minutes.

Table 7.

Time (min.)	15	30	45	60	90	120
Current efficiency (%)	55.8	49.3	41.2	35.7	28.5	22.9

Now, what will be the results of supplying the materials which are being consumed during electrolysis? As the first step, 0.5 g. of borax which is the calculated amount to recover the same consumed for the perborate production is added in five equal portions at 15, 30, 45, 60, and 90 minutes after the beginning of electrolysis. The current efficiency of 120 minutes' electrolysis is then 25.4%, being a small improvement of the original value.

Secondly, besides addition of borax, carbon dioxide is supplied which is assumed to be lost during electrolysis. When the gas is kept passing up in the electrolyte, coming out of a tube at the bottom of the cell, the inner diameter of which tube is 3.5 mm., at the rate of about 50 bubbles per minute, the current efficiency is 18.6% for the electrolysis of the same period as above. When carbon dioxide is passed in, the other conditions remaining the same as before, for every other 15 minutes, the current efficiency is 24.5%. Among several other results, the highest current efficiency, 27.3%, is obtained by supplying the gas into the solution so as just check its coming out of the tube for 5 minutes each half an hour. The current efficiency of 5 hours' electrolysis under the same conditions as last-mentioned is 12.0%.

Summary.

(1) It is shown that under certain conditions there is no distinction between electrolysis with diaphragm and that without it as regard to the current efficiency of perborate production and it is possible to disuse diaphragm without affecting the current efficiency.

(2) The presence of a comparatively large amount of potassium chromate is harmful to the perborate production. When present in a small amount, however, it is not harmful but, then, advantage owing to its presence is not so considerable as was generally accepted.

(3) Effects of adding potassium sulphate and potassium chloride are studied.

(4) Current efficiency is increased, when a solution containing sodium carbonate and borax is electrolysed, by replenishing borax and carbon dioxide.

(5) Electrolyses of metaborate solutions, rates of thermal decomposition of percarbonate and perborate solutions as well as stability of perborate in the course of electrolysis are studied and consequently it is concluded that perborate is probably, in the electrochemical process, a secondary product of the anodic reaction, the primary one being percarbonate.

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