

EXPERIMENTS ON THE ELECTROLYTIC REDUCTION OF POTASSIUM CHLORATE

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When a solution of potassium chlorate is subjected to electrolysis with use of copper electrodes a remarkably high electrical reduction efficiency is gained. At the suggestion of Professor Bancroft I have made a study of the conditions best suited to this reduction, at the same time attempting to obtain insight into its character.

The problem is of especial interest in that a principle is involved which, it seems probable, will prove of general application in the carrying out of useful reduction processes.

By varying singly the different factors involved, a series of results are obtained from which the conditions for maximum reduction are readily deduced. After a general description of experimental details these results will be taken up.

Except in the experiments intended to test the effect of change of concentration, the chlorate solution used contained 50 g of KClO_3 to the liter. The chlorate used contained the faintest trace only of chloride. For each experiment 450 cc of the solution was measured into a beaker of 500 cc capacity. The beaker was supported in a water-bath.

The electrodes were cut from sheet copper. One of these, usually the anode, was rotated. This mode of stirring proved very convenient, saving the space of separate apparatus and being quite efficient. In this way also both surfaces of the anode shared equally in the action. On account of the presence of additional resistance in the circuit the rotation did not cause appreciable fluctuation in the current. A mercury cup on the stem of the rotating electrode furnished means of contact.

The current used was taken from a 110 volt circuit. In the earlier experiments this was measured by an ammeter, reading to tenths of amperes, or by a voltmeter used as an ammeter, all

runs being timed. Later a copper voltameter was also placed in series. Error due to its previous absence is within that resulting from other uncontrolled factors.

The amount of reduction was estimated by gravimetric determination of the chloride formed, this being the sole product of the reduction of the chlorate. In the electrolysis of an undivided solution of potassium chlorate using copper electrodes, a dark brown precipitate, essentially copper oxide, forms; this is mixed with particles of lighter color which are probably an oxychloride. The cathodes are slightly blackened, while the anodes are rapidly consumed, what remains of them being coated with oxide and peculiarly pitted; the pits are filled with cuprous chloride. The precipitates were dissolved and the anodes cleaned by dilute nitric acid, the solutions gained being added to the main solution and the whole filtered and made up to a definite volume. From this portions were taken for analysis.

Usually two reductions were carried out at the same time, those experiments being made in series, the results of which were to be directly compared or contrasted.

The "percentage efficiencies" used are electrical efficiencies on the basis that for 100 percent one molecule of KClO_3 will be reduced by 3×26.8 ampere hours.

The variables that are considered as determining the yield are anode and cathode densities, temperature, concentration and ampere hours. A compact tabulation of results may be of service in their discussion:

With anodes of 5×10 cm and 2×10 cm, other conditions being the same, the cathodes in each case 5×10 cm, the average reduction efficiencies are 140 pct and 176 pct respectively. In a shorter run anodes of 2×10 cm and 0.41 cm diameter (latter a copper wire, the solution was stirred by attached glass rods) gave efficiencies of 200 pct and 175 pct. The efficiency, then, increases markedly with increase of anode current density, a maximum being reached when the density is very high.

Using cathodes of 5×10 cm, 2×10 cm, and 1×10 cm,

the percentages are 140 pct, 144 pct, and 139 pct respectively. Within a wide range the extent of reduction appears independent of the current density at the cathode.

The temperature usually chosen was that reached through a

No.	Anode	Cathode	Amperes	Hours	Temp.	Conc.	Series with	Efficiency
1a	5×10 cm	5×10 cm	4	2	94°-96°	50	2a	136.2
b	"	"	"	"	"	"	3a	147
c	"	"	"	"	"	"	4	137.8
							av.	140.3
2a	2×10 cm	"	"	"	"	"	1a	173.3
b	"	"	"	"	"	"	3b	179.4
							av.	176
3a	5×10 cm	2×10 cm	"	"	"	"	1b	132
b	"	"	"	"	"	"	2b	155.5
							av.	143.8
4	"	1×10 cm	"	"	"	"	1c	138.7
5a	"	5×10 cm	"	3	"	"	5b	85.1
b	"	"	"	"	"	"	5a	78.7
							av.	81.9
6a	"	"	"	1.5	"	"	6b	95.9
b	"	"	"	"	"	"	6a	96.6
							av.	96.3
7a	2×10 cm	"	"	0.5	"	"	7b	196
b	"	"	"	"	"	"	7a	204
							av.	200
8a	0.41 cm dia	"	"	"	"	"	8b	174.4
b	"	"	"	"	"	"	8a	175.4
							av.	174.9
9	2×10 cm	"	"	1	"	"	10	189.1
10	"	"	"	"	"	100	9	189.7
11a	"	"	"	"	62°-63°	50	11b	184.6
b	"	"	"	"	"	"	11a	189.7
							av.	187
12a	"	"	"	"	37°-39°	"	12b	149.2
b	"	"	"	"	"	"	12a	135
							av.	142

bath of boiling water, slightly elevated, about 2°, by the heating effect of the current, that is 94°-96°. An experiment of which the efficiency at this temperature was 189 pct, duplicated

at 62° – 63° gave 187 pct, and at 37° – 39° , 142 pct. Between about 62° and 96° , an unexpectedly wide range, the efficiency is constant, while that for 37° – 39° shows a marked falling off. At this lower temperature the blue hydrated copper oxide at first separates and gradually darkens, changing to brown.

The efficiency is, within the limits tried, independent of the concentration of the chlorate solution. Solutions of 50 g and 100 g KClO_3 to the liter gave efficiencies of 189 pct and 190 pct.

With constant current the yield decreases as the length of the run increases. Runs of one-half, one, and two hours duration, other factors being constant, gave 200 pct, 189 pct, and 176 pct. On account of the formation of cuprous chloride and of copper oxychloride (?) the solution gradually becomes alkaline. The decreasing rate of reduction is in part due to the free alkali formed. On initially adding 10 cc of sodium hydroxide solution, containing approximately 1 g NaOH to 15 cc of its solution, to the chlorate solution, the yield was decreased from 171 pct to 112 pct. Using a greater amount of the caustic soda solution, 20 cc and 30 cc respectively, there was practically no reduction of chlorate. The anodes were but slightly attacked and there was a vigorous evolution of gas at each electrode, which is not the case without free alkali initially added.

Summary of the foregoing results:

In the electrolytic reduction of potassium chlorate in solution, using copper electrodes, the anode not being placed in a separate compartment, a yield approaching 200 pct is readily gained, and this percentage appears to be the maximum. This efficiency can be obtained over a wide range of temperature and of concentration. It is favored by a high current density at the anode and is independent of the cathode current density. The efficiency is rapidly cut down by the presence of free alkali and this is slowly formed during the course of the electrolysis.

The explanation that first suggests itself for this extraordinary efficiency is that a large fraction of the yield of chloride

is simply the result of spontaneous decomposition of the chlorate itself, or of one of its reduction products. The temperature of the water-bath and the presence of finely divided copper oxide and of certain amounts of copper salts in solution would favor such action.

As a result of spontaneous decomposition there must be either evolution of oxygen or simultaneous formation of a higher oxidation product, that is, of a perchlorate. In the experiments tabulated above there is little or no gas evolved from the anodes, none from the main body of the liquid and a momentary evolution only, of hydrogen from the cathodes, this seeming to cease when the copper oxide begins to separate. Tests made for perchlorate yield negative results. Moreover neither boiling a solution of chlorate of the strength used with copper sulphate nor heating it on the water-bath with finely divided copper oxide, causes it to break down to chloride. These facts show plainly that the hypothesis of direct spontaneous decomposition is untenable.

It is conceivable that our high efficiency rests upon a change in valence of the copper which dissolves from the anode. If the copper goes into solution in cuprous form subsequently becoming further oxidized, an efficiency of 200 pct might be realized. This, however, would necessitate a loss in weight at the anode equal to twice the increase in weight of the copper voltameter cathode. In runs one-half hour in length the loss is, indeed, 1.6 times the weight of copper deposited in the voltameter. But when the time is extended to two hours the two weight differences are approximately equal, and this without great falling off of efficiency. This, then, as an explanation, must also be set aside.

The rapid destruction of the copper anode and the initial, but momentary, evolution of hydrogen at the cathode would be in accord with the formation of intermediate reduction products at the anode, which are further reduced by the hydrogen, absorbing it. The assumption of reduction taking place at the anode is unusual, its validity is, however, readily tested.

If such an action takes place we would expect that on separating the anode and cathode liquids by a membrane or porous cup, hydrogen would be continuously evolved from the cathode and the anode electrolyte would give evidence of the intermediate products of reduction, probably through the giving off of oxygen with formation of a chloride. A trial of this was made through two experiments carried out in series, each being arranged as follows: An unglazed clay cell was placed in a 500 ccm beaker. 450 ccm of the chlorate solution was distributed between the two compartments. A copper anode, 2×10 cm, was inserted in the cell. A cathode of like dimensions was rotated in the outer compartment. A current of four amperes was allowed to pass for half an hour. The temperature was 94° – 96° .

From the outset, and continuing through the experiments, there is a vigorous evolution of hydrogen from the cathodes, but no bubbles of gas rise from the anode liquid. About the cathode the liquid remains almost colorless, being slightly brown at the close. Here there is no, or at most very slight, formation of chloride. In the anode compartments, on the other hand, the reduction is marked, giving a heavy precipitate of cuprous chloride as the chief product. The anode liquids become blue, showing the presence in solution of some copper salt. There is, however, no trace of chlorites or of hypochlorites to be found in this liquid and these cannot have spontaneously decomposed, giving rise to the chloride, for as above noted, no oxygen is set free. The chlorate that undergoes reduction here must, therefore, pass directly to chloride. The hydrogen cannot play the rôle tentatively assigned to it. Determinations of the chloride formed in the cathode compartments show efficiencies of 73 pct and 76 pct respectively.

In these last experiments the anode liquids differed from those in which no cell was used in becoming acid instead of faintly alkaline. To eliminate this difference and so make more positive the proof of anode reduction under the conditions of the first series, other experiments were carried out in which caustic

soda solution, made by the action of sodium on water and free from chloride, was added in small portions to keep the liquid as nearly as possible neutral. Otherwise the detail of arrangement was as described above.

Here too the reduction was noteworthy, though instead of cuprous chloride copper oxide was precipitated, the chief amount of chloride formed remaining in solution. There was no evidence of the chlorate being reduced in steps. Each of two trials gave an efficiency of 58 pct.

The acid or alkaline reaction of the solution was determined by litmus paper. In order to prevent great increase of volume it was necessary to use a rather strong solution of sodium hydroxide. On this account it was possible only to approach neutrality, the solution being much of the time slightly alkaline, and as previously shown the presence of free alkali in sufficient amount completely prevents reduction. It is probable that with more perfect means of neutralization the efficiency would be considerably higher than found.

The marked difference in the action at the cathode according to whether or not this electrode is contained in a porous cell, not being readily explicable through any change which takes place in the chlorate, appears to be connected with the copper which goes into solution from the anode. This points to an analogy with the results obtained by Binz¹ in the electrolytic reduction of indigo.

Binz finds that with use of a zinc anode in caustic soda solution reduction of suspended indigo to indigo white takes place at the anode by direct action of the metal. And further that by dissolving zinc in an alkaline cathode electrolyte in which indigo is suspended, the reduction is about 15 times as great as takes place without the zinc, the trials being made in series. Repeating with use of soluble coloring matters Binz and Hagenbach² obtained like results and conclude that reductions attributed to nascent hydrogen are frequently better explained

¹ *Zeit. Elektrochemie*, 5, 5, 103 (1898).

² *Ibid.* 6, 261 (1899).

as direct reductions by metals. The same principle underlies the process patented by the firm of C. F. Boehringer and Son¹ for the reduction of nitrobenzene to aniline. This is effected through use of a tin cathode, or of an indifferent cathode and addition of a tin salt to the cathode compartment, from which the anode is separated by a membrane. Later they find that the tin may be replaced by certain other metals, as copper, lead and iron. By this method is gained an almost quantitative reduction of nitrobenzene to aniline hydrochloride.

A. Chilesotti² has recently extended these results and has called attention to the importance of the methods of Boehringer and Son. He regards the spongy metal which is deposited on the cathode during the reduction as the active agent, but states that the reduction cannot be ascribed to the catalytic action of this metal, since when the reduction of a portion of nitrobenzene with tin is complete all of the tin is precipitated, but on adding a fresh portion of nitrobenzene tin again passes into solution.

To test whether this theory of Binz would apply to the case in hand, an experiment was devised in which 10 g of crystals of pure copper sulphate were initially added to the chlorate solution about the cathode. Reduction at the anode was prevented by inserting the latter in a porous cell containing a solution of potassium sulphate. The electrodes were of sheet copper, the size being 2×10 cm. The cathode was rotated. The temperature was that of the water-bath and a current of four amperes was passed for half an hour. At the outset no bubbles rise from either electrode. The anode liquid assumes a deep blue color and the anode is split into a number of layers between which a white substance is deposited. The cathode liquid, originally blue in color, from the copper salt added, becomes almost colorless. A heavy deposit of cuprous chloride forms mixed with a yellow substance which also coats the electrode.

¹ German Patent, 116942, 117007 (1900).

² Zeit. Elektrochemie, 7, 768 (1901).

Analysis shows an efficiency of 91 pct, and this confined to the cathode compartment where under like conditions, but in absence of the copper salt, no reduction takes place. The result, therefore, is in harmony with the experiments of Binz.

When the reduction was confined to the anode the efficiency was 58 pct. This added to that just obtained for the cathode gives 149 pct as a total. It seems probable that this sum with greater accuracy in securing comparable conditions would approach the maximum of 200 pct, found for the corresponding case in which simultaneous reduction is allowed to take place, no cell being used. Assuming that under like conditions the sum of the separate efficiencies would equal the joint efficiency, the most apparent cause of discrepancy lies in the free acid and alkali respectively present when the electrodes are separated.

The substance reduced in the above experiments is an electrolyte, while the investigations of Binz and the processes of Boehringer and Son deal immediately with non-electrolytes.

In the reduction of nitrobenzene it was seen that there is a choice between using a cathode of a particular metal or of using an indifferent cathode and a salt of the metal dissolved in the cathode electrolyte. At the temperatures employed with potassium chlorate in solution the simple use of a copper cathode is not sufficient to cause reduction.

Previous use has not been made, as far as the writer has discovered, of simultaneous reduction at anode and cathode. And the only instance of anode reduction noted is that in which Binz effects the change of indigo to indigo white in alkaline solution by the direct action of a zinc anode. In his subsequent work, however, Binz makes use of a porous cell.

Disregarding the higher efficiency attainable, the doing away with the necessity of two liquids in many, particularly organic, reductions would in itself make possible a decided saving in time and material.

The fact that spontaneous decomposition of the chlorate is not one of the factors and that the passage from chlorate to

chloride seems to be direct, renders it highly probable that the result is general. This will be determined by further experiments.

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