

**315.** *Studies in Electrolytic Oxidation. Part VIII. Apparent Reducing Properties of an Anode.*

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IN previous parts of this series (Glasstone and Hickling, J., 1932, 2345, 2800; 1933, 829; 1934, 10, 1772, 1878; 1936, 820) the view has been put forward that, at an anode in aqueous solution, hydrogen peroxide is formed by combination of discharged hydroxyl radicals. If this is the case, it might be expected that an anode would exhibit some of the apparent reducing properties of hydrogen peroxide, notably in reducing acidified solutions of potassium permanganate and dichromate. Large effects are not to be anticipated, since the rate of spontaneous decomposition of the peroxide at an anode is high, and there is the possibility that any reduction which takes place may be masked by reoxidation, either electrically or by nascent oxygen. This has now been investigated and the predicted effects, although small, have been observed.

\* Indicates analyses by Synthetical and Analytical Laboratories, Ltd.

## EXPERIMENTAL.

The general method adopted in the investigation was to collect the oxygen evolved at the anode under consideration along with the hydrogen formed at the cathode of a separate voltameter connected in series, and to show that the oxygen-hydrogen ratio is greater than that expected for the decomposition of water, thus indicating that reduction of the anolyte has occurred.

The electrolytic apparatus consisted of two voltameters connected in series; each was formed from a jar of about 110 c.c. capacity, fitted with a rubber stopper carrying an electrode, a narrow gas delivery tube, and a wide tube, provided at the lower end with a tight filter-paper plug, which served as the second compartment of the voltameter. The first voltameter, from which the hydrogen was collected, was filled with 2*N*-sulphuric acid throughout the experiments. The cathode, housed in the main jar, was of stout platinum-foil 1 cm. square, and the anode in the subsidiary tube was of platinum wire; the anode gas was not collected. The second voltameter, from which the oxygen was collected, contained in the jar 100 c.c. of the anolyte under investigation, and the small compartment was filled with 2*N*-sulphuric acid. Anodes of various sizes were used, the small ones being made of platinum wire and the large ones of platinum-foil. The cathode in the subsidiary tube was of platinum wire, and the cathode gas was not collected. The cathode gas from the first voltameter and the anode gas from the second were led along a Y-tube to a small mercury trough.

All electrolyses were carried out at room temperature at a fixed current of 0.10 amp., the *C.D.* being varied by changing the size of the anode. Before each electrolysis, the platinum anode was cleaned with warm concentrated hydrochloric acid, warm concentrated nitric acid, and water, and heated to redness. A preliminary electrolysis of 3 hours was carried out in each experiment in order to saturate the electrolytes and to displace the air from the voltameters. 20 C.c. samples of the mixed anode and cathode gases were then collected at intervals of 1 hour, transferred to a Bone-Newitt apparatus, and analysed by exploding with excess oxygen. From the original pressure of the gas and the contraction on explosion, the initial ratio of oxygen to hydrogen present was worked out. Control experiments with sulphuric acid alone as anolyte were made at frequent intervals.

*Results.*—*Potassium permanganate.* The solutions were made up by weight in small quantities from A.R. potassium permanganate. Evolution of oxygen by spontaneous decomposition was found in all cases to be inappreciable under the conditions of electrolysis. The following results were obtained for electrolysis at various *C.D.*'s with (A) *N*-potassium permanganate in 2*N*-sulphuric acid and (B) 2*N*-sulphuric acid alone, as anolyte.

<i>C.D.</i> , amp./sq. cm.	0.10.	0.05.	0.01.	0.0036.
	O <sub>2</sub> /H <sub>2</sub> ratio.			
(A) 3 Hours' electrolysis .....	0.559	0.658	0.636	0.551
4 " " .....	0.567	0.657	0.641	0.543
Mean .....	0.563	0.658	0.639	0.547
(B) 3 Hours' electrolysis .....	0.456	0.484	0.482	0.496
4 " " .....	0.457	0.481	0.486	0.492
Mean .....	0.457	0.483	0.484	0.494

In all cases the oxygen-hydrogen ratio when the permanganate anolyte is used is considerably greater than the theoretical value of 0.500 for the decomposition of water. (The departure from this value in the case of the sulphuric acid alone at the higher *C.D.*'s is presumably due to persulphate formation.) There appears to be an optimum *C.D.* of about 0.03 amp./sq. cm. at which the oxygen-hydrogen ratio is a maximum for the permanganate anolyte. With the strongly acidified permanganate solutions used, no oxide deposition on the anode was observed, in general.

To find the effect of varying the permanganate concentration, electrolyses were carried out at a *C.D.* of 0.05 amp./sq. cm. with various concentrations in 2*N*-sulphuric acid. The results are given below :

Concentration of KMnO <sub>4</sub> , <i>N.</i>	1.0.	0.5.	0.1.	0.02.
	O <sub>2</sub> /H <sub>2</sub> ratio.			
3 Hours' electrolysis .....	0.658	0.631	0.541	0.518
4 " " .....	0.657	0.619	0.549	0.521
Mean .....	0.658	0.625	0.545	0.520

It is evident that the extent of the reduction falls off rapidly with decreasing concentration of permanganate.

To show that the general effect is not due to the sulphuric acid electrolyte, electrolyses were also carried out in perchloric and phosphoric acid solutions. Some results are given below; a *C.D.* of 0.05 amp./sq. cm. was employed, and the anolyte was (A) *N*-potassium permanganate in the acid specified, and (B) the acid alone.

	Electrolyte.	2 <i>N</i> -H <sub>2</sub> SO <sub>4</sub> .	2 <i>N</i> -HClO <sub>4</sub> .	2 <i>M</i> -H <sub>3</sub> PO <sub>4</sub> .
			O <sub>2</sub> /H <sub>2</sub> ratio.	
(A) 3 Hours' electrolysis	.....	0.658	0.658	0.568
4 " " "	.....	0.657	0.654	0.576
Mean	.....	0.658	0.656	0.572
(B) 3 Hours' electrolysis	.....	0.484	0.498	0.494
4 " " "	.....	0.481	0.496	0.496
Mean	.....	0.483	0.497	0.495

In all the cases studied the oxygen-hydrogen ratio with permanganate is markedly greater than 0.500. Close agreement between the values in the various electrolytes is not to be expected, since the acidity may vary somewhat from one solution to another, and the acids may have specific actions on the decomposition of hydrogen peroxide and the reaction of the peroxide with permanganate. Actually, the values for the sulphuric and the perchloric acid electrolytes are very similar, while that for the phosphoric acid solution is much lower. In this connexion it was noted that solutions of permanganate in phosphoric acid kept exceptionally well over a period of months, and it seems not improbable that both this and the result of the electrolytic experiment may be due to the removal by the phosphoric acid of manganous ions, which act as catalysts for both the autodecomposition and the reaction with hydrogen peroxide.

*Potassium dichromate.* The solutions were made up by weight from A.R. salt. As the reduction of acidified dichromate by hydrogen peroxide is comparatively slow, it was expected that the increase of the oxygen-hydrogen ratio above 0.500 would be much less than in the case of permanganate. This is borne out by the following results obtained for electrolysis at various *C.D.*'s with (A) *N*-potassium dichromate in *N*-sulphuric acid and (B) *N*-sulphuric acid alone, as anolyte.

	<i>C.D.</i> , amp./sq. cm.	0.10.	0.05.	0.01.	0.0036.
			O <sub>2</sub> /H <sub>2</sub> ratio.		
(A) 3 Hours' electrolysis	.....	0.514	0.515	0.520	0.523
4 " " "	.....	0.517	0.516	0.524	0.526
Mean	.....	0.515	0.516	0.522	0.525
(B) 3 Hours' electrolysis	.....	0.490	0.499	0.498	0.500
4 " " "	.....	0.494	0.497	0.498	0.500
Mean	.....	0.492	0.498	0.498	0.500

It is seen that a small but definite increase in the oxygen-hydrogen ratio occurs when dichromate is present. The effect apparently increases somewhat with decreasing *C.D.* over the range studied. In all the electrolyses of dichromate solutions the platinum anode remained clean and bright.

The effect of varying the dichromate concentration was found by carrying out electrolyses at a *C.D.* of 0.0036 amp./sq. cm. in solutions which were *N* with respect to sulphuric acid. The results are given below :

	Concentration of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , <i>N</i> .	1.0.	0.5.	0.25.	0.1.
			O <sub>2</sub> /H <sub>2</sub> ratio.		
3 Hours' electrolysis	.....	0.523	0.511	0.507	0.503
4 " " "	.....	0.526	0.509	0.507	0.497
Mean	.....	0.525	0.510	0.507	0.500

Reduction falls off rapidly with decreasing concentration of dichromate.

In alkaline solution hydrogen peroxide does not reduce chromate, but on the contrary oxidises chromic salts. An electrolysis was therefore carried out at a *C.D.* of 0.0036 amp./sq. cm. with a solution of *N*-potassium dichromate in *N*-potassium hydroxide as anolyte. The results are given on p. 1456; the similar experiment with *N*-potassium dichromate in *N*-sulphuric acid as anolyte is inserted for comparison.

	Electrolyte.	N-KOH.	N-H <sub>2</sub> SO <sub>4</sub> .
3 Hours' electrolysis .....		0.500	0.523
4 " " .....		0.497	0.526
Mean.....		0.499	0.525

As expected, the oxygen-hydrogen ratio with the alkaline anolyte is normal.

#### DISCUSSION.

As predicted by the theory, the paradoxical phenomenon of an anode, which is a strong oxidising agent, bringing about reduction with evolution of oxygen, occurs in the case of acid permanganate and dichromate solutions. It may be supposed that at the anode hydroxyl ions are discharged and the resulting radicals combine irreversibly in pairs to give hydrogen peroxide. The greater part of this then decomposes spontaneously, but a small proportion may react with the permanganate or dichromate, leading to evolution of oxygen and simultaneous reduction. The reaction of hydrogen peroxide with dichromate is comparatively slow, and so here the effect is less marked than with the permanganate solution. As the concentration of either the permanganate or the dichromate is decreased, the speed of the reduction will be diminished, and hence a greater proportion of the peroxide will tend to decompose spontaneously, until ultimately in dilute solution the reduction will not be able to compete at all effectively with the decomposition. As the *C.D.* is raised, the concentration of hydrogen peroxide at the anode will increase, and both the spontaneous decomposition and the reaction with the anolyte will therefore be accelerated. The relative extent to which the two rates are changed will determine how the reduction is influenced by *C.D.* If the rate of decomposition increases more rapidly with peroxide concentration than does the speed of reduction, then the reduction will fall off with increasing *C.D.*, while if the order is reversed then the reduction will diminish with decreasing *C.D.* In certain circumstances it is apparent that there may be an optimum *C.D.* at which the reduction is a maximum.

Various other theories could be advanced to account for the phenomena under discussion, but all are apparently *ad hoc*. For instance, it might be suggested in the case of permanganate that a metallic peroxide is formed on the anode surface which reacts with the anolyte in a manner analogous to hydrogen peroxide; it is difficult to see how this would account for the observations with dichromate, however. Alternatively, it might be supposed that permanganate and dichromate ions are discharged at the anode, and that the resulting radicals then react mainly with water to give oxygen and form the corresponding acids, but that there is also a tendency for them to decompose giving oxygen and lower metallic oxides. Against this view it can be argued that there is no evidence that permanganate and dichromate ions, along with many other anions, are ever discharged at an anode (see Glasstone and Hickling, "Electrolytic Oxidation and Reduction," pp. 36-38, 1935), and if any process of the above type did occur, it might be expected to be found with other highly oxidised anions, such as perchlorate, and this does not seem to be the case. Although none of these theories appears to be inherently probable, yet it is not possible conclusively to reject them without further investigation.

#### SUMMARY.

1. In the electrolysis of acidified potassium permanganate and dichromate solutions, the volume of oxygen obtained at a platinum anode is greater than that expected for the decomposition of water. The influence of *C.D.*, concentration, and certain other factors has been investigated.

2. The effect is attributed to the apparent reducing action of hydrogen peroxide, primarily formed at the anode, upon the permanganate and dichromate solutions.

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