67. *Studies in Electrolytic Oxidation. Part IX. The Anodic Oxidation of Chromic Salts to Chromates.*

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THE electrolytic oxidation of chromic salts to chromic acid and chromates was recorded by Regelsberger (*Z. angew. Chem.*, 1899, **12**, 1123; *Z. Elektrochem.*, 1899, **6**, 308; see also Elbs, *ibid.*, 1899, **6**, 388; Haüssermann, *Z. angew. Chem.*, 1893, **6**, 363), and later investigated by Müller and Soller (*Z. Elektrochem.*, 1905, **11**, 863; see also Levi and Ageno, *Atti R. Accad. Lincei*, 1906, **15**, ii, 549, 615); since that time investigation of the process has been mainly concerned with its industrial utilisation (Askenasy and Révai, *Z. Elektrochem.*, 1913, **19**, 344; McKee and Leo, *Ind. Eng. Chem.*, 1920, **12**, 16; Drozdov, *J. Gen. Chem. Russia*, 1933, **3**, 345; see also Roudnick, *Z. Elektrochem.*, 1929, **35**, 249; Takegami, *Bull. Chem. Soc. Japan*, 1930, **5**, 16) and little has been done to elucidate its mechanism. The process may be formulated as an electrical change involving the transfer of electrons, $Cr^{\cdot\cdot\cdot} + 4H_2O = CrO_4'' + 8H^{\cdot} + 3e$, or it may be supposed that oxygen is first formed at the anode and then brings about chemical oxidation. Neither of these simple views will account, however, for the recorded peculiar features of the oxidation, notably that the process only occurs efficiently in acid solution at a lead dioxide anode, and scarcely at all at an anode of smooth platinum. It appeared of interest, therefore, to reinvestigate the process and to see if any light could be thrown upon it by the theory of electrolytic oxidation developed in the previous parts of this series (Glasstone and Hickling, J., 1932, 2345, 2800; 1933, 829; 1934, 10, 1772, 1878; 1936, 820; Hickling, J., 1936, 1453).

EXPERIMENTAL.

The electrolytic apparatus consisted of two 150-c.c. beakers, forming the anode and cathode compartments respectively, connected together by a wide glass siphon containing electrolyte, the ends of the siphon being stopped by tight filter-paper plugs. This arrangement was found to have a reasonably low electrical resistance, but completely prevented mixing of anolyte and catholyte, and avoided the possibility of impurities introduced by the use of a porous pot. The anolyte was usually 100 c.c. of 0·1*M*-chromium potassium sulphate in 0·5*N*-sulphuric acid, and for the catholyte 100 c.c. of *N*-sulphuric acid were used in each case; the siphon was filled with either *N*-sulphuric acid or saturated potassium sulphate solution according to whether an acidic anolyte was used or not. For most of the experiments a rectangular platinum sheet anode of area 20 sq. cm. was used; this was mounted vertically, and rotated at 160 r.p.m. Prior to use, the anode was cleaned with warm concentrated hydrochloric acid, warm concentrated nitric acid, and water, and heated to redness. A platinum-foil cathode was employed. Current was supplied from a 40-volt battery through rheostats and a milliammeter. In each experiment 720 coulombs of electricity were passed, and the anode solution was then analysed. Except where otherwise stated, all electrolyses were carried out at room temperature, *i.e.*, *ca.* 20°.

A.R. Chromium potassium sulphate, $Cr_2(SO_4)_3,K_2SO_4,24H_2O$, and A.R. sulphuric acid were used for preparing the anolyte. Since the violet colour of the solution interfered to some extent with the observation of the end-point in the iodometric estimation of the chromate formed, the solutions were boiled and cooled before use, the colour being thereby changed to green. Check experiments showed that both the violet and the green solutions gave identical results on electrolysis. The quantity of electricity passed was such as to give 100 c.c. of 0·025*M*-chromate if the oxidation took place with 100% efficiency. After electrolysis, the chromate was estimated by strongly acidifying measured portions of the solution, adding excess potassium iodide, and titrating with standard thiosulphate. The efficiencies were in general reproducible to 1—2%.

Results.

(In the following experiments, a "stock solution" is one of 0·1*M*-chromium potassium sulphate in 0·5*N*-sulphuric acid.)

Influence of C.D.—The influence of *C.D.* was investigated by electrolysing a stock solution with the smooth platinum anode, various currents being employed. The following results were obtained:

C.D., amp./sq. cm.	0·02	0·01	0·005	0·0025	0·001	0·0005
Efficiency, %	1	1	2	4	29	35

It is seen that the efficiency of the oxidation at a smooth platinum anode in acid solution is very low at moderate *C.D.*'s, but becomes appreciable when the *C.D.* is greatly reduced.

Influence of Temperature.—The following results were obtained at a number of temperatures with the smooth platinum anode and stock solution at a *C.D.* of 0·01 amp./sq. cm.

Temperature	20°	31°	51°	58°	69°	88°
Efficiency, %	1	21	47	57	77	77

The efficiency evidently rises rapidly with increasing temperature.

Effect of Acidity and Alkalinity.—The effect of varying acidity and alkalinity is shown by the results below, the smooth platinum anode being employed with a *C.D.* of 0·01 amp./sq. cm. Solutions of 0·1*M*-chromium potassium sulphate were made up in 0·5*N*-sulphuric acid, water, and 0·5*N*-potassium hydroxide respectively. 1 G. of calcium carbonate was added to each 100 c.c. of the water solution to act as a buffering agent and prevent its becoming strongly acid on electrolysis. The alkaline solution was slightly turbid.

Medium.	0·5*N*-H_2SO_4.	H_2O.	0·5*N*-KOH.
Efficiency, %	1	63	77

It is apparent that the oxidation at a platinum anode is greatly favoured by working in neutral and alkaline solutions.

Influence of Anode Material.—In order to determine the influence of anode material, a stock solution was electrolysed with a *C.D.* of 0·01 amp./sq. cm. with various anodes, the size, shape, and apparent area of each being the same as that of the smooth platinum. Prior to use, the platinised platinum anode was cleaned and washed as above; it was then subjected to cathodic or anodic polarisation in *N*-sulphuric acid at a *C.D.* of 0·025 amp./sq. cm. for 1 hour, or its oxygen content controlled by rotating it in 0·01*N*-potassium permanganate in p_H 9 borate buffer for 30 minutes (see Glasstone and Hickling, J., 1932, 2347). These treatments yielded different results, which are recorded. The gas-carbon anode was washed with warm water before use. The lead dioxide anode was made from lead sheet and was anodically polarised at 0·025 amp./sq. cm. for 1 hour in *N*-sulphuric acid. The results are given below.

Anode material.	Efficiency, %.	Anode material.	Efficiency, %.
Smooth Pt	1	Platinised Pt :	
PbO_2	100	Cathodically polarised	97
Gas C	1	Controlled	53
		Anodically polarised	43

The lead dioxide anode gives the theoretical efficiency of oxidation, and the smooth platinum and the gas-carbon anode give very little chromate. The behaviour of platinised platinum is of particular interest, cathodic polarisation greatly increasing, and anodic polarisation decreasing, the oxidation efficiency. This is the opposite of what has been observed in some other cases of electrolytic oxidation (cf. Glasstone and Hickling, J., 1933, 830).

Influence of Concentration.—Experiments were made in which the concentration of chromium potassium sulphate in 0·5*N*-sulphuric acid was varied. The controlled platinised platinum anode was used with a *C.D.* of 0·01 amp./sq. cm. The results are below :

Concn. of $Cr_2(SO_4)_3,K_2SO_4$, *M*	0·02	0·05	0·1	0·2
Efficiency, %	20	36	53	66

The efficiency increases with increasing chromium-ion concentration.

Influence of Anions.—The effect of foreign anions was studied by carrying out electrolyses with stock solution to which various salts had been added. The controlled platinised platinum anode was used with a *C.D.* of 0·01 amp./sq. cm. The following results were obtained.

Substance added.	(None.)	KNO_3, 0·1*N*.	KH_2PO_4, 0·1*N*.	$KClO_4$, satd.	KF, 0·1*N*.	H_3BO_3, 0·1*N*.
Efficiency, %	53	61	62	64	76	50

It is seen that all the strong electrolytes increase the efficiency somewhat, the effect of fluoride being particularly marked, whereas boric acid has no appreciable effect.

To see if chromium salts other than the sulphate could be anodically oxidised to chromate, electrolyses were carried out with the nitrate in nitric acid, and the perchlorate in perchloric acid as electrolytes. The electrolytic conditions were as above, and the following results were obtained.

Electrolyte.	Efficiency, %.
0·1*M*-$Cr_2(SO_4)_3,K_2SO_4$ in 0·5*N*-H_2SO_4	53
0·2*M*-$Cr(NO_3)_3$ in 0·5*N*-HNO_3	60
0·2*M*-$Cr(ClO_4)_3$ in 0·5*N*-$HClO_4$	86

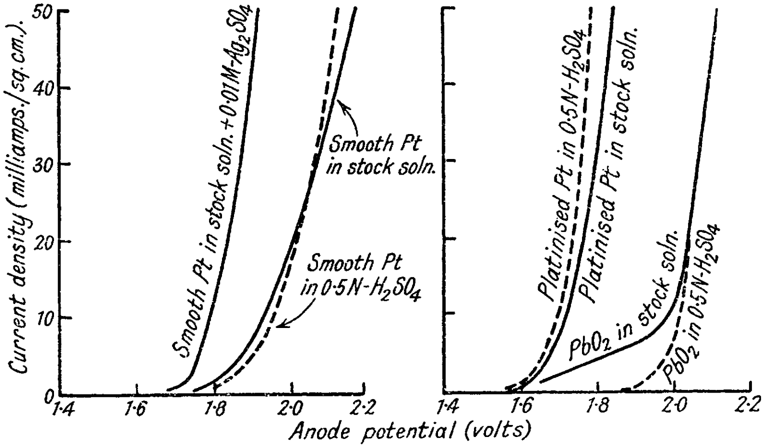
Influence of Catalysts for Hydrogen Peroxide Decomposition.—The influence of catalysts for hydrogen peroxide decomposition was found by adding various metallic sulphates and oxides to the anolyte. Two sets of experiments were carried out: (*a*) with the usual acid stock solution, and (*b*) with an initially neutral 0·1*M*-chromium potassium sulphate solution containing 1 g. per 100 c.c. of calcium carbonate to act as a buffering agent and prevent the solution becoming very acid on electrolysis. The smooth platinum anode was used with a *C.D.* of 0·01 amp./sq. cm.

Catalyst.	Efficiency, %. Acid solution.	Efficiency, %. Neutral solution.
(None)	1	63
$CuSO_4$, 0·01*M*	2	40
$FeSO_4$, 0·01*M*	2	27
$CoSO_4$, 0·01*M*	8	31
$MnSO_4$, 0·01*M*	7	17
„ 0·1*M*	19	

Catalyst.	Efficiency, %. Acid solution.	Efficiency, %. Neutral solution.
$PbSO_4$, satd.	70	96
Ag_2SO_4, 0·01*M*	97	87
„ 0·001*M*	95	
PbO_2, 0·5 g./100 c.c.	93	
MnO_2, 0·5 g./100 c.c.	5	

In general, oxide deposits were observed on the anode when electrolytes containing lead, manganese, or silver salts were used. It is to be noted that in acid solution all the catalysts for hydrogen peroxide decomposition raise the efficiency of the oxidation, the effect being particularly marked with lead and silver compounds; in neutral solution, however, except in the cases of lead and silver salts, the catalysts decrease the efficiency markedly. This peculiar result will be discussed later.

Potential Measurements.—In order to make measurements of the potentials at which the oxidation occurs, a small stationary platinum anode of area 0·1 sq. cm. was used, and its potential at a series of currents measured against that of a saturated calomel electrode by the potentiometer–voltmeter method. Experiments were carried out with (*a*) the smooth platinum anode in 0·5*N*-sulphuric acid, in stock solution, and in stock solution containing 0·01*M*-silver sulphate severally, (*b*) the anode coated with lead dioxide in 0·5*N*-sulphuric acid and in stock solution, and (*c*) the platinised anode in 0·5*N*-sulphuric acid and in stock solution. In each case the anode was pre-polarised at a *C.D.* of 0·02 amp./sq. cm. for 15 minutes in the solution to be used, in order that a steady state might be attained before observations were made. The potentials were then measured at a series of increasing *C.D.*'s, and immediately afterwards a repeat experiment was carried out. In general, the results were reproducible within about 2 centivolts. The values are given in the diagrams in the form of *C.D.*–potential curves, the potentials being expressed on the hydrogen scale.



Chemical Oxidation of Chromic Compounds.—The chemical oxidising action of the substances likely to be formed at an anode was investigated.

Oxygen. Gaseous oxygen was bubbled for 3 hours through boiling 0·1*M*-chromium potassium sulphate solutions made up in 0·5*N*-sulphuric acid, water, and 0·5*N*-potassium hydroxide severally. No trace of chromate was formed in any case.

Hydrogen peroxide. Quantities of 20-vol. hydrogen peroxide, containing available oxygen equivalent to that formed at an anode by the passage of 720 coulombs of electricity, were added to 100-c.c. lots of 0·1*M*-chromium potassium sulphate made up in 0·5*N*-sulphuric acid, water (containing 1 g. of calcium carbonate), and 0·5*N*-potassium hydroxide severally, and the solutions boiled until all the peroxide was decomposed (as indicated by testing with titanium sulphate). The solutions were then examined for chromate, and the results expressed as efficiencies.

Medium.	Acid.	Neutral.	Alkaline.
Oxidation efficiency, %	0	12	29

Metallic peroxides. Quantities of silver (Ag_2O_2 prepared by Jirsa's method, *Z. anorg. Chem.*, 1925, **148**, 130), lead, and manganese peroxides, containing available oxygen equivalent to that formed in the electrolysis, were added to 100 c.c. portions of 0·1*M*-chromium potassium sulphate made up in 0·5*N*-sulphuric acid, water (containing 1 g. of calcium carbonate), and 0·5*N*-potassium hydroxide, and the mixtures boiled for 3 hours; the solutions were then filtered, and the chromate formed estimated.

	Oxidation efficiencies, %.		
	Acid.	Neutral.	Alkaline.
Ag_2O_2	87	23	10
PbO_2	42	15	47
MnO_2	14	4	8

DISCUSSION.

The experimental results seem to indicate conclusively that the electrolytic oxidation of chromic ions to chromate is not a purely electrical, reversible process, represented by the equation $Cr^{\cdot\cdot\cdot} + 4H_2O = CrO_4'' + 8H^{\cdot} + 3e$. Such a process should be characterised by a definite oxidation–reduction potential, and provided that potential can be attained the oxidation should be largely independent of variable factors such as anode material, temperature, addition of catalysts, etc. In the present case the *C.D.*–potential curves show no sign of any definite potential associated with the reaction; on the contrary, the oxidation takes place efficiently at a platinised platinum anode at a low potential and scarcely at all at a smooth platinum anode at a much higher potential. Many other such anomalies can be quoted. The potentials at which the oxidation takes place seem to be merely oxygen evolution values. It may be noted that attempts to measure the static potential of the chromate–chromic ion system have given unsatisfactory results (see Winter and Moyer, *J. Amer. Chem. Soc.*, 1935, **57**, 1402; Kolthoff, *Chem. Weekblad*, 1919, **16**, 450; Luther, *Z. physikal. Chem.*, 1899, **30**, 653).

The simple view that oxygen is first formed at the anode and then brings about chemical oxidation seems equally unsatisfactory. The chemical experiments show that gaseous oxygen does not oxidise chromic ions, and the *C.D.*–potential curves show no substantial depolarisation for oxygen Even if it is supposed that the oxygen is activated in some way by the electrode material, it seems impossible to explain such results as the effect of acidity and alkalinity, the influence of pre-polarisation on the platinised platinum anode, and the fact that catalysts such as manganese, cobalt, and copper sulphates have opposite effects in neutral and in acid solution.

All the results, however, can be accounted for if the view is adopted that hydrogen peroxide is primarily formed at an anode in aqueous solution by the irreversible combination of discharged hydroxyl radicals, and if the observations are then interpreted in terms of the experimentally ascertained properties of this peroxide and the metallic peroxides which are known to be formed in certain circumstances. The chemical experiments show that hydrogen peroxide oxidises chromic ions to chromate in alkaline solution, also in neutral solution to a less extent, but in acid solution brings about no oxidation—on the contrary it reduces any chromate present. It would, therefore, be expected that *under conditions such that no alternative oxidising agent is formed*, the efficiency of oxidation should be high in alkaline solution, less in neutral solution, and negligible in acid solution. This corresponds precisely to the observed efficiencies with a smooth platinum anode at moderate *C.D.*'s.

For a complete interpretation of the experimental results with various electrode materials and in the presence of catalysts for hydrogen peroxide decomposition, it is necessary to take into account the observed oxidising action of the metallic peroxides which may be formed. The following schemes will represent the possibilities for alkaline or neutral, and for acid solutions.

Alkaline and neutral solutions.

$$2OH' + 2\oplus = 2OH \longrightarrow \underset{\substack{\downarrow \\ \text{Oxidises chromic} \\ \text{ions to chromate.}}}{H_2O_2} \longrightarrow H_2O + \underset{\substack{\downarrow \\ \text{May oxidise chromic ions to chromate} \\ \text{through formation of metallic peroxide.}}}{O} \longrightarrow \tfrac{1}{2}O_2 \text{ (Oxygen evolved)}$$

Acid solution.

$$2OH' + 2\oplus = 2OH \longrightarrow \underset{\substack{\downarrow \\ \text{Reduces chromate} \\ \text{to chromic ions.}}}{H_2O_2} \longrightarrow H_2O + \underset{\substack{\downarrow \\ \text{May oxidise chromic ions to chromate} \\ \text{through formation of metallic peroxide.}}}{O} \longrightarrow \tfrac{1}{2}O_2 \text{ (Oxygen evolved)}$$

From the first scheme it is seen that in neutral solution a catalyst for hydrogen peroxide decomposition should reduce the oxidation efficiency at a smooth platinum anode unless there is formed at the same time a metallic peroxide which is itself a better oxidising agent for chromic salts than is hydrogen peroxide. In agreement with this it is found that copper, cobalt, ferrous, and manganous sulphates all markedly reduce the oxidation efficiency in neutral solution; of these, only manganese gives a visible peroxide deposit on the anode, and, as shown experimentally, manganese peroxide in neutral solution has only comparatively slight oxidising action on chromic salts. On the other hand, silver and lead salts give rise to peroxide deposits on the anode, and these, although good catalysts for hydrogen peroxide decomposition, are themselves, as shown experimentally, excellent oxidising agents. The oxidation efficiency is therefore raised.

In acid solution, as depicted in the second scheme, the state of affairs is quite different. Here, not only does hydrogen peroxide not oxidise chromic salts, but it tends to reduce any chromate which may be formed. In acid solution, therefore, any factor tending to decompose hydrogen peroxide will tend to increase oxidation efficiency, and the maximum effect will be obtained if, at the same time, a metallic peroxide which is a good oxidising agent can be formed. From the experimental results this is seen to be the case. Silver, lead, and (to a less extent) manganese salts, all of which are catalysts for hydrogen peroxide decomposition and can form peroxides which are oxidising agents, increase the efficiency markedly; other catalysts, such as copper and cobalt salts, which do not form oxide deposits on the anode, increase it slightly.

The influence of anode material can be explained in a similar way. Lead dioxide, which is a good catalyst for hydrogen peroxide decomposition and also a good oxidising agent, gives the highest efficiency. Gas carbon is a fairly good catalyst for hydrogen peroxide decomposition but lacks oxidising properties and therefore gives a low efficiency. The case of platinum requires special mention. It seems probable that an oxide can be formed on the platinum surface which slowly oxidises chromic salts to chromate. With smooth platinum at ordinary temperatures the process is too slow to give an appreciable efficiency of oxidation at normal *C.D.*'s; at very low *C.D.*'s, however, a larger fraction of the anodic oxygen can be utilised in this way and the efficiency of oxidation increases. A similar result may be brought about by raising the temperature, whereby the process is accelerated and at the same time the decomposition of hydrogen peroxide is favoured.* Platinised platinum is a good catalyst for hydrogen peroxide decomposition, and presents an enormously increased area for the oxidation; hence, high efficiencies are observed. Cathodic polarisation increases the catalytic power of platinum for hydrogen peroxide decomposition, but anodic polarisation decreases it (Spitalsky and Kagan, *Ber.*, 1926, **59**,

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* It might be suggested that the increase in oxidation efficiency at low current densities or elevated temperatures is due to increased chance of diffusion of chromic salt to the anode. The *C.D.* employed, however, seems to be considerably less than that for limiting diffusion conditions, and the theory meets with many additional difficulties.

2905); it would, therefore, be expected that cathodic polarisation should favour, and anodic polarisation decrease, the oxidation efficiency in acid solution, as is found to be the case. It is interesting to note that poisoning of the platinised platinum electrode decreases the oxidation efficiency; with the stock solution and the controlled platinised platinum anode at a *C.D.* of 0·01 amp./sq. cm., the oxidation efficiency was reduced from 53 to 37% by making the platinising solution 0·01*M* with respect to mercuric chloride.

SUMMARY.

1. A comprehensive investigation has been made of the anodic oxidation of chromic salts: the influence of *C.D.*, of temperature, of acidity and alkalinity, of anode materials (smooth and platinised platinum, lead dioxide, and gas carbon), of concentration, of anions, and of catalysts for hydrogen peroxide decomposition, has been studied.

2. The current efficiency for the formation of chromate at a smooth platinum anode is high in alkaline and in neutral solutions, but negligible in acid solution, unless either very low *C.D.*'s are employed or the temperature is raised. Lead dioxide and platinised platinum anodes give good efficiencies in acid solution, the amount of oxidation in the latter case being greatly affected by previous treatment of the electrode; gas carbon gives a very low efficiency. Small amounts of the sulphates of copper, cobalt, iron, and manganese markedly lower the efficiency of oxidation at a smooth platinum anode in neutral solution, but in acid solution they increase it. Silver and lead sulphates raise the efficiency considerably in both neutral and acid solutions.

3. The anode potentials were measured under a variety of conditions, and appear to be merely oxygen evolution potentials. There seems to be no relation between anode potential and efficiency of oxidation.

4. It is shown that the observations made in the present work cannot be accounted for by a purely electrical oxidation mechanism, and an alternative theory, involving the primary formation of hydrogen peroxide at the anode, is advanced.

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