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ELECTRODE PROCESSES

IV

Mechanism of Oxidation of Chlorate to
Perchlorate at the Platinum Anode

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MECHANISM OF OXIDATION OF CHLORATE TO PERCHLORATE AT
THE PLATINUM ANODE

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ABSTRACT

On the basis of the results of electrolytic and chemical oxidation experiments with chlorate solutions a mechanism was postulated for the electrolytic oxidation of chlorate to perchlorate at a platinum anode. It was proposed that platinum(VI) oxide forms at the anode surface under the conditions favorable for chlorate oxidation and that an intermediate species is formed between the oxide and chlorate ions. The intermediate species then decomposes into platinum(IV) oxide and perchlorate ions. Mechanisms proposed by earlier observers were discussed with reference to their failure to explain satisfactorily the experimental results.

INTRODUCTION

Electrolytic Preparation of Perchlorates.

Perchlorate was first produced electrolytically by Stadion in 1816¹, and shortly afterwards the same investigator discovered perchloric acid by allowing sodium chlorate to react with concentrated sulfuric acid. The first important paper appeared in 1898, in which Foerster² outlined a set of conditions for obtaining high current yields of perchlorate. Many papers have since appeared in which improvements have been made in the technical aspects of the process. Important considerations and present practice may be summarized as follows with respect to the important variables:

Electrolyte.

Current yields of perchlorate increase with increased chlorate concentration.^{2,3} The efficiency remains at a high level until a major part of the chlorate has been oxidized, then falls off rapidly. It has been proved desirable to keep the hydroxyl ion concentration low to minimize current losses that would attend the discharge of hydroxyl, chloride, and hypochlorite ions.⁴ The trend in commercial perchlorate production is toward the use of more concentrated sodium chlorate solutions (5.6 M) which are slightly acid. Apparently only the Cardox Corporation process

¹ Referred to by F. Winteler, Z. Elektrochem., 5, 49 (1898).

² F. Foerster, Z. Elektrochem., 4, 386 (1898).

³ F. Winteler, Z. Elektrochem., 5, 217 (1898).

⁴ N. V. S. Knibbs and H. Palfreeman, Trans. Faraday Soc., 16, 402 (1920).

employs a slightly alkaline electrolyte.⁵

Influence of electrolyte additives.

Current efficiency in the oxidation of chlorate with a lead dioxide anode was increased from 41% to 70% by the addition of sodium fluoride to the electrolyte.⁶ This result was attributed to the fact that the addition of fluoride increased the already high oxygen overvoltage of the lead dioxide anode. The presence of phosphoric acid in the electrolyte reduced perchlorate yields at a platinum anode. Perchlorate formation actually ceased when only a small amount of chlorate was present. Under constant conditions (current density and temperature) a nearly straight line relation was found between the remaining chlorate and the phosphate present.⁷ The most important additives used in modern perchlorate cells are soluble chromates. It is claimed that chromates increase perchlorate yields by forming protective films on the cathode thereby preventing cathodic reduction of chlorate to chloride.⁸

Temperature.

Lower temperatures favor perchlorate formation. Above 60 degrees C. current yields are low^{2,3} and at 80-100 degrees C. there is no perchlorate formation.^{3,9} At low current densities (e.g., 10 amps per dm²), the current efficiency is markedly reduced by increasing temperature, but this effect

⁵Technical Report to the Office of Naval Research, Contract Nonr-372(00), The Pennsylvania Salt Mfg. Co., August 31, 1951.

⁶S. Kitahara and T. Okanga, J. Electrochem. Assoc. (Japan) 10, 409 (1942)

⁷R. A. Miro', O. J. Garcia, and M. G. Serveri, Anales real. soc. espan. fis. y quim. 47B, 17 (1951).

⁸J. C. Schumacher, Trans. Electrochem. Soc. 92, 45 (1947). (review)

⁹W. Oechsli, Z. Elektrochem. 9, 807 (1903).

is much less noticeable at higher current densities (e.g. 15 amps per dm^2).¹⁰ At even higher current densities such as 45 to 50 amperes per dm^2 no adverse effect on current efficiency was observed¹¹, up to 60 degrees C. Because of better power yields, present practice is to use temperatures in the range 40-55 degrees even though slightly higher current yields could be obtained at a lower temperature.⁵

Agitation.

Adequate agitation is necessary for high perchlorate yields. Special cells have been designed to improve agitation.⁵

Current density.

Current yields of perchlorate are highest at high current densities.^{4,9,11} The actual current density used in commercial operation varies considerably; however, perchlorate cells in the United States operate with a current density of over 30 amperes per dm^2 .

Anode materials.

Smooth platinum anodes give the highest current yields of perchlorate. Thus, smooth platinum is used as the anode material in most perchlorate cells.⁵ Lead dioxide anodes can also be used for perchlorate production, however, the yield is not as high as with smooth platinum.¹² On the other hand, platinumized platinum is unsuitable because it gives low current yields of perchlorate.³

Because of the high initial cost of platinum and the fact that it corrodes slightly, an extensive search is being made for a suitable substitute for platinum. All of the common and many of the more rare metals,

¹⁰E. Blau and R. Weingand, Z. Elektrochem. 27, 1 (1921).

¹¹J. G. Williams, Trans. Faraday Soc., 15, 134 (1920).

¹²G. Angel and H. Mellquist, Z. Elektrochem., 40, 702 (1934).

except those of the platinum group, were found to corrode very rapidly when used as anodes in a sodium chlorate electrolyte.¹³ Other anode materials, while having suitable physical properties, were unsuitable because of the low or negligible perchlorate yield obtained under the most favorable circumstances e.g. tungsten¹⁴, molybdenum¹⁴, artificial magnetite¹³, graphite^{15,16}, palladium¹⁷, tantalum¹⁷, stainless steel¹⁷, Hastelloys¹⁷, Nicrome-V¹⁷, and manganese dioxide^{17, 18}.

Chemical Synthesis of Perchlorate

Essentially three types of chemical reactions lead to the production of Perchlorate: (1) thermal auto-oxidation of chlorates, (2) decomposition of chlorates by strong acids, and (3) direct chemical oxidation. Considerations applying to those processes are of some interest in connection with the mechanism of anodic oxidation.

Thermal auto-oxidation.

Potassium chlorate, as well as other alkali chlorates, undergoes auto-oxidation when heated to just above its melting point, according to

¹³H. O. Howard, Trans. Am. Electrochem. Soc., 43, 51 (1923).

¹⁴G. Angel, Z. Elektrochem., 40, 641 (1934).

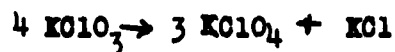
¹⁵V. Sikvonen, Suomen Kemistilehti, 10B, 27 (1937).

¹⁶H. C. Schock and R. H. Pritchett, U. S. Patent 1,279,593 (Sept. 24, 1918), report that carbon preferably impregnated with molten paraffin, ceresin, or osakerite when used in a diaphragm cell gives a current efficiency of at least 50% for perchlorate formation.

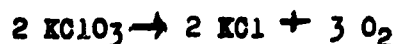
¹⁷J. W. Hackett and M. A. Fineman, Dept. of Chemistry, Providence College Technical Report to the Office of Naval Research, Contract Nonr-1213(00), December 31, 1953.

¹⁸Perchlorate was produced only when the manganese dioxide was plated on platinum.

the equation



In addition, a decomposition reaction, having no essential connection with the auto-oxidation reaction, takes place according to the equation^{19,20}



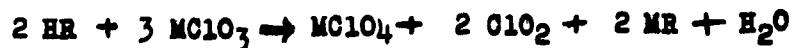
Several oxides, such as silver(I) oxide, lead(IV) oxide and barium peroxide have been reported to serve as catalysts for the auto-oxidation reaction.²¹ However, there is more recent evidence that tends to disprove the earlier observations; there is no proved catalytic agent for the auto-oxidation reaction^{22,23}.

Nothing is known to inhibit the oxygen producing reaction²⁴, but many substances, such as bases, manganese(IV) oxide and copper(II) oxide are known to catalyze this reaction.

Under ideal conditions as much as 90 percent of the theoretical yield of potassium perchlorate may be obtained²⁵.

Decomposition of chlorates with strong acids.

Chlorates are decomposed by strong concentrated acids, such as sulfuric, nitric, phosphoric and chromic acid, according to the equation



¹⁹W. H. Sodeau, J. Chem. Soc., 81, 1066 (1902).

²⁰J. Scobai, Z. physik. chem., 44, 319 (1903).

²¹G. J. Fowler and J. Grant, J. Chem. Soc., 57, 272 (1890).

²²F. C. Mathers and J. W. H. Aldred, Trans. Am. Electrochem. Soc., 42, 285 (1922).

²³W. Farmer and J. B. Firth, J. Chem. Soc., 125, 82 (1924)

²⁴W. D. Bancroft and J. E. Magoffin, J. Franklin Inst. 224, 298 (1937).

²⁵F. Meyer, German Pat. 300,713 (Aug. 30, 1919).

where M is the metal and R is the acid radical. Yields of perchlorate range from 10-30% of the theoretical value. Acids which yield no perchlorate are formic, trichloroacetic, hydrofluoric, hydrochloric, chloric, peroxydisulfuric, permanganic (20%), arsenic (50%), acetic (glacial), monochloroacetic, oxalic (saturated solution), tartaric (25%) and lactic acid (25%)²⁶.

Direct chemical oxidation.

The literature pertaining to the direct chemical oxidation of chlorate to perchlorate is fragmentary and at times contradictory. It has been demonstrated that such strong oxidizing agents as oxygen exposed to ultra violet light²⁷, ozone^{27,28}, 30 percent hydrogen peroxide²⁷, potassium permanganate²⁷, and sodium peroxide²⁷ do not lead to the formation of appreciable amounts (>2%) of perchlorate. It is generally considered that peroxydisulfate without a catalyst yields no perchlorate^{26,30}. Of all the oxidizing agents reported in the literature, only lead(IV) oxide²⁹ and peroxydisulfate with silver ion catalyst²⁷ give appreciable perchlorate yields.

Mechanism for the Anodic Oxidation of Chlorate to Perchlorate.

Four possible mechanisms have been proposed for the anodic oxidation of chlorate to perchlorate.

²⁶V. Lenher, H. W. Stone, and H. H. Skinner, J. Am. Chem. Soc., 44, 143 (1922)

²⁷O. W. Bennett and M. L. Mack, Trans. Electrochem. Soc. 29, 323 (1916).

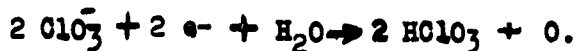
²⁸W. Z. Oeschall, Z. Elektrochem. 9, 807 (1903).

²⁹Ehrhardt (I.G. Farben), "Kalium Perchlorat", Department of Commerce Office of Technical Service P. B. Report No. 73283 Frames 503-7.

³⁰Bennett and Mack²⁷ obtained a 17.69% yield of perchlorate on boiling for an hour a 5% sodium chlorate solution containing an excess of sodium peroxydisulfate.

Disproportionation mechanism.

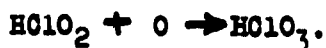
In the earliest mechanism proposed it was assumed that chlorate ion discharge is the primary process, followed by the reaction of the discharged radical with water to form chloric acid



Because of the high chloric acid concentration, presumably existing at the electrode, it disproportionates to form perchloric acid according to



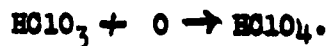
followed by



Arguments in favor of this mechanism and against the active oxygen theory to follow are: (a) that perchlorate formation takes place less readily in alkaline solution, and (b) that no perchlorate is obtained on treating chlorate solutions directly with ozone.

Active oxygen mechanism.

In the active oxygen mechanism it was proposed that the chlorate is oxidized directly to perchlorate by active oxygen formed at the anode



Arguments in favor of the active oxygen mechanism and against the earlier mechanism are as follows:

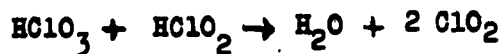
(a) At an iron anode perchlorate formation begins at a potential far below that necessary for chlorate ion discharge³¹ (0.023 volts vs. N. C. E.),

(b) Chlorate can be oxidized chemically to perchlorate under conditions where the formation of free chlorate radicals is highly improbable.

(c) The free chlorous acid formed would react with the chloric acid

³¹E. P. Schoch, Phys. Chem. 14, 735 (1910).

present evolving chlorine dioxide



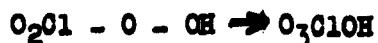
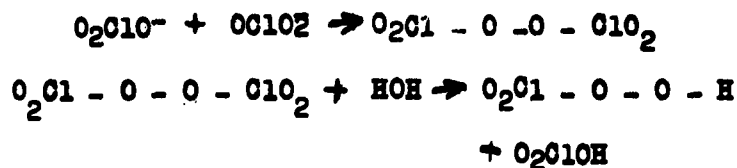
The evolution of chlorine dioxide has never been observed during this process.

(d) There is no direct evidence that chlorous acid is formed when strong chloric acid decomposes.

(e) The increase in the dissociation of water with rise in temperature is insufficient to account for the large decrease in efficiency with rise in temperature. In the active oxygen theory the effect of temperature on perchlorate formation is due to a decrease in the active oxygen concentration at the anode. Increasing the temperature decreases the active oxygen concentration.

The Peroxide mechanism.⁴

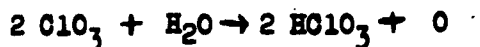
This mechanism was proposed on the basis of a superficial similarity between the production of perchlorate and peroxydisulfate.



The first reaction is analogous to the formation of peroxydisulfuric acid $\text{O}_2(\text{OH})\text{S} - \text{O} - \text{O} - \text{S}(\text{OH})\text{O}_2$. The peroxide reacts with water in the second reaction and rearranges to a more stable form in the third equation. The objections to the active oxygen mechanism in favor of the peroxide mechanism are:

(a) The decrease in efficiency with rise in temperature should follow the decrease of overvoltage; however, this is not the case. In the peroxide theory the effect of high temperature on decreasing perchlorate yield is due to the increased rate of oxygen producing side reactions

such as

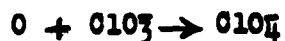


and also on the fact that high temperatures increase hypochlorite and hydroxyl ion discharge owing to increased mobility.

(b) The active oxygen theory does not satisfactorily explain the effect of alkalinity on efficiency.

(c) The oxidation of chlorate by active oxygen producing reagents is inconclusive.

(d) According to the active oxygen theory the efficiency of perchlorate formation should decrease with increasing current density. Actually the efficiency increases with increasing current density. The active oxygen produced at the anode is used up in the two reactions



The former results in gaseous oxygen liberation and loss of efficiency, while the latter results in perchlorate formation. During the electrolysis of a chlorate solution the concentration of active oxygen on the anode will be such as to make the velocities of the two reactions just sufficient to account for all the oxygen discharged. Now, if the current is increased, the active oxygen concentration will increase until the two velocities have risen sufficiently to balance the extra oxygen discharged. Since the first reaction rate is proportional to the square of the active oxygen concentration it will increase to a greater extent than the second reaction, thereby decreasing the efficiency for perchlorate formation.

Additional suggestion.

The most recent suggestion as to the mechanism for perchlorate for-

nation postulates an intermediate X at the anode surface³². On the basis of polarisation curves, at a platinum anode perchlorate formation takes place at a higher potential than that required for oxygen evolution. As the anode potential is increased there appears an inflection in the polarisation curve at which point perchlorate formation begins.

Based on chemical and electrochemical studies, this work was undertaken in order to provide a better understanding as to the mechanism by which chlorate is oxidised to perchlorate at an anode surface.

³²A. Ruis, J. Llopis and M. C. Servert, *Anales real. soc. espan. fis. y quim. (Madrid)*, 49B, 455 (1953).

EXPERIMENTAL DETAILS

Electrolytic Apparatus

Apparatus for the anodic oxidation of chlorate consisted of a 400 ml beaker containing an unglazed porcelain porous cup of 52 mm. diameter and 100 mm. height which served as the anode compartment. In all electrolysis experiments circulation of the anolyte was maintained by using an air stirrer with a glass propeller.

Gold and platinum anodes comprised 1 cm. x 1 cm. sheets which were fabricated from 0.002 inch thick sheet metal. Each anode was provided with a small tab to which a wire lead of the same material was connected by folding the tab over the wire and pressing the tab securely against the wire.

For the lead(IV) oxide anode a 1 cm. x 1 cm. sheet of nickel was electroplated with lead(IV) oxide. The electrode had a stem 2 mm. wide and 12 cm. long, plated in the same way, which served as a support. A smooth adherent oxide plate was obtained by electroplating for 8 hours at 30 degrees C. and at a current density of approximately 5 milliamperes per cm². The electrolyte was prepared by dissolving lead(II) oxide in aqueous sodium hydroxide and sodium potassium tartrate.³³

The graphite anode was prepared by coating National spectrographic carbon rods, 3/16 inch diameter, with Ucilon (United Chromium Inc. protective coating material) with the exception of an area of 2 cm². The rod was inserted into a tightly fitting Pyrex glass tube and cemented in place in such a

³³J. H. Mellquist, U. S. Patent 1,595,675 (August 10, 1926).

way as to expose the uncoated surface to the electrolyte.

Platinum cathodes, 1 cm. x 1 cm. were used in all experiments and both the anodes and cathodes were supported by a glass bridge. In those experiments using a current of 0.1 amperes the quantity of electricity was determined with a copper coulometer. In experiments using a higher current, the quantity of electricity was calculated from the product of the current and the time of electrolysis. Current was measured with a Triplet model 420 ammeter. For the first six electrolysis experiments the current was furnished by two 6 volt storage batteries connected in series. In subsequent experiments a 1 kw., 28.5 volt DC generator was used.

All electrolysis experiments were done at 30 degrees C. $\pm$ 0.5 degrees C. The anolyte comprised 100 ml. of solution and the catholyte, 150 ml. of 0.5 M sulfuric acid solution. In experiments in which the anolyte was initially basic, 1 M sodium hydroxide solution was used in place of the sulfuric acid.

Percent yields were calculated from the ratio of the number of moles of perchlorate actually produced to the number of moles of perchlorate theoretically obtained if all the available oxygen produced at the anode went into perchlorate formation.

Chemical Oxidation Experiments

In the initial experiments, the effects of various oxidizing agents on sodium chlorate were determined by testing for the presence of perchlorate qualitatively with methylene blue. Experiments were done using 10 ml. of aqueous 5 M sodium chlorate and 3.5 M sulfuric acid. Sufficient oxidizing

agent was used theoretically to oxidize about one half of the chlorate to perchlorate. The catalytic effect of various substances on the oxidation of chlorate with peroxydisulfate was also determined. In each experiment approximately one-half gram of proposed catalyst was added to the chlorate solution, followed by addition of peroxydisulfate. Reactions were carried out, with stirring, for 36 hours at a temperature of 40 degrees C.

In later experiments quantitative determinations of perchlorate were carried out. For each oxidizing agent at least two experiments were done, one with 10 ml. of aqueous 3 M chloric acid and the other with 0.047 moles of solid sodium chlorate added to 10 ml. of 9 M sulfuric acid solution. In one group of experiments the temperature was maintained at 30 degrees C. while the oxidizing agent was added slowly and with stirring. Reaction was allowed to continue for 48 hours. Other experiments were done at 65 degrees C. in 3 M chloric acid solution, the oxidizing agent being added after the solution had reached 65 degrees C. An attempt to heat the sodium chlorate-sulfuric acid mixture to 65 degrees C. resulted in violent decomposition, thus experiments using this mixture at that temperature were discontinued. In order to avoid undue evaporation of chloric acid, reaction time at 65 degrees C. was limited to 24 hours. In all experiments the chlorate was in excess of the oxidizing agent.

The yield of perchlorate was calculated from the number of equivalents of oxidizing agent used. Those oxidizing agents which produced significant amounts of perchlorate are listed in Table 1, together with their purity, method of analysis, and reduction product. In some cases a previously unopened bottle of a commercially available reagent was used and the oxidation equivalent was calculated from the reported assay.

Chloric acid was prepared by slowly adding the stoichiometric quantity of 9 M sulfuric acid solution to concentrated, aqueous barium chlorate at

room temperature with vigorous stirring. Small portions of sulfuric acid or barium chlorate were added until the chloric acid contained a slight excess of barium ion. The precipitated barium sulfate was then removed by centrifugation followed by filtration through a fine sintered-glass filter. The filtrate was evaporated under vacuum at 40 degrees C. to give 3 M chloric acid, which was stored in an amber colored reagent bottle. Other reagents, which were prepared by methods reported in the literature, were: platinum(IV) oxide 1-hydrate³⁴, platinum(IV) oxide 4-hydrate³⁵, silver(II) oxide³⁶, nickel(III) oxide³⁷, bismuth(IV) oxide³⁸, cobalt(III) oxide³⁹, uranium peroxide 2-hydrate⁴⁰, barium ferrate(VI)⁴¹, silver(II) -dipyridyl perchlorate⁴². All other compounds were reagent grade chemicals and they were used without further purification.

³⁴"Organic Synthesis", collective Vol. 1, A. H. Blatt, Ed., John Wiley and Sons, New York, 1941, p. 463.

³⁵L. O. Morgan and W. H. Philipp, Dept. of Chemistry, University of Texas, Technical Report to the Office of Naval Research, Contract No. Nonr 375(04) September, 1955. No. 5, p. 6.

³⁶"Inorganic Synthesis", Vol. IV, J. C. Bailar, Jr., Ed., McGraw-Hill Book Co., Inc., New York, 1953, p. 12.

³⁷J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 15, Longmans, Green and Co., New York, 1936, p. 398.

³⁸R. R. Worsley and P. W. Robertson, J. Chem. Soc. (trans.) 117, 63 (1920).

³⁹Reference 37, Vol. 14, 1935, p. 589.

⁴⁰G. W. Watt, S. L. Achorn and J. L. Marley, J. Am. Chem. Soc., 72, 3341 (1950).

⁴¹J. R. Gump, W. F. Wagner, J. M. Schreyer, Anal. Chem. 26, 1957 (1954).

⁴²G. A. Barbieri and A. Malaguti, Atti. acad. nazl. Lincei, Rend. classe sci. fis., mat. e nat., 8 619 (1950).

Analytical Reagents and Methods

Qualitative determinations of perchlorate were carried out using methylene blue reagent⁴³, which was prepared by mixing 0.1 ml. of 1.6% methylene blue solution with 25 ml. of 50% zinc sulfate solution.

Samples to be tested were first made basic with sodium hydroxide in order to precipitate the cations; the insoluble materials were then removed by centrifugation. In cases in which peroxydisulfate was used, the solution was boiled for a few minutes to decompose the peroxydisulfate, which interferes with the test. Before adding the methylene blue reagent the samples were neutralized by addition of dilute sulfuric acid.

The test for perchlorate was carried out by adding 0.5 ml. of saturated potassium nitrate solution and 15 ml. of methylene blue reagent to 1 ml. samples. The resulting solutions were stirred and allowed to stand for 15 minutes before examination. Perchlorate concentrations were estimated by comparison of the test solutions with standard samples prepared in a similar fashion.

A volumetric method was used in the quantitative determinations of perchlorate⁴⁴ which involved determination of chlorate and total chlorate and perchlorate, perchlorate concentration being found by difference. In the presence of perchlorate, the preferential reduction of chlorate to chloride was accomplished with iron(II) sulfate⁴⁵ in a dilute sulfuric acid

⁴³F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis", Vol. 2, D. Van Nostrand Co., Inc., New York, 1949, p. 720.

⁴⁴The Pennsylvania Salt Mfg. Co., Technical Report to the Office of Naval Research, Contract Nonr 372(00), August 31, 1951, Part II, p. 51.

⁴⁵Because of the red coloration produced with iron(II) sulfate and the dipyriddy complex the reduction of chlorate to chloride in these samples was carried out with sodium hydrogen sulfite and a small amount of iron(II) sulfate. The addition of a little nitric acid to the reduced sample before titration completely eliminated the red color.

solution. Chlorate and perchlorate were reduced simultaneously to chloride in a dilute sulfuric acid solution with titanium(III) sulfate and a small amount of iron(II) sulfate. Prior to analysis, interfering cations were removed by precipitation with sodium hydroxide. In each case chloride was determined volumetrically by the Volhard method.

Available oxygen in the various oxides was determined by thermal decomposition⁴⁶. Oxygen evolved from decomposition of the oxide was swept out of the reaction chamber with carbon dioxide which was then absorbed in concentrated potassium hydroxide solution. The oxygen volume was measured in an inverted glass buret. The accuracy of the method was found to be about 3% as determined using potassium chlorate as a standard.

⁴⁶S. Altmann and R. H. Busch, Trans. Faraday Soc., 45, 720 (1949).

RESULTS

Electrolysis Experiments

Experiments were done with smooth platinum and graphite anodes using as electrolyte 0.5 M sodium chlorate solution, 1 M in sodium hydroxide or 0.5 M in sulfuric acid. In one set of experiments sodium fluoride was added to the electrolyte in order to increase the anode potential⁴⁷. The presence of this material in the anolyte had little influence on the yield of perchlorate.

In acid electrolytes the graphite anodes disintegrated rapidly, especially at the higher current densities. As the electrode disintegrated the current dropped; however, in experiments at 0.1 ampere the current was kept constant by regulation of the potential. In experiments carried out at 0.5 amperes, the graphite anode disintegrated so rapidly that even though the potential was increased to a maximum of 12 volts the final current dropped to 0.15 amperes. Perchlorate yields, together with the electrolysis conditions, are given in Table 2.

In order to reduce the number of different ions present in the electrolyte, subsequent experiments were done using 1 M chloric acid solution as the anolyte. For each of the four anode materials tried, experiments were carried out at currents of 0.1 and 0.5 amperes, the number of Faradays used being approximately equal. Results of these experiments are shown in Table 3.

As was the case in previous experiments, the graphite electrode disintegrated rapidly, especially at 0.5 amperes, and at the same time the

⁴⁷A. Hickling and S. R. Richards, J. Chem. Soc., 256 (1940).

TABLE 2

Perchlorate yield as a function of anode material and anolyte composition. Current: 0.1 ampere; temperature: 30 degrees C.

Anode	Anolyte	Quantity of current (Faradays)	Perchlorate yield (millimoles)	Perchlorate yield (percent of theoretical)
Pt. (smooth)	0.5 M NaClO ₃ 1.0 M NaOH	0.0527	0	0
	0.5 M NaClO ₃ 0.5 M H ₂ SO ₄	0.0527	15	55
	0.5 M NaClO ₃ 1.0 M NaOH 0.5 M NaF	0.0369	(trace)	< 3
	0.5 M NaClO ₃ 0.5 M H ₂ SO ₄ 0.5 M NaF	0.0369	10	54
Graphite	0.5 M NaClO ₃ 1.0 M NaOH	0.0473	(trace)	< 3
	0.5 M NaClO ₃ 0.5 M H ₂ SO ₄	0.0473		0
Graphite	0.5 M NaClO ₄ 1.0 M NaOH	0.03*	(trace)	< 3
	0.5 M NaClO ₃ 0.5 M H ₂ SO ₄	0.03*	(trace)	< 3

*Current was initially 0.5 amperes but dropped to a final value of 0.15 amperes

TABLE 3

Perchlorate yield as a function of anode material and current density.

Temperature: 30 degrees C.; anolyte: 1 M HClO_3 solution.

Anode	Current (amperes)	Quantity of electricity (Faradays)	Perchlorate yield (millimoles)	Perchlorate yield (percent of theoretical)
Pt(smooth)	0.1	0.0579	2	7
	0.5	0.0559	18	64
Au(smooth)	0.1	0.0579	0	0
	0.5	0.0559	(trace)	<3
PbO_2	0.1	0.0579	0	0
	0.5	0.0559	3	11
Graphite	0.5*	0.03	(trace)	<3

*This figure represents the initial current. The current dropped to a final value of 0.15 amperes while the anode disintegrated rapidly.

potential had to be increased in order to maintain constant current. In experiments done at 0.5 amperes the graphite electrode disintegrated so rapidly that it was impossible to prevent the current from dropping to 0.15 amperes.

After electrolysis had proceeded for a short time a brown film formed on the gold anode; however, the electrode remained intact throughout the electrolysis. The lead(IV) oxide coated electrode held up quite well under the conditions of electrolysis. There was a slight stripping off of the oxide plate toward the end of electrolysis at the higher current, nevertheless, the oxide covering was heavy enough to keep the nickel base well covered throughout the experiment. No visible film was seen on the platinum electrode after electrolysis.

Chemical Oxidation Experiments

The efficiency of some chemical oxidizing agents for perchlorate formation was determined under a variety of conditions. Qualitative experiments showed that no perchlorate was produced by such strong oxidizing agents as potassium peroxydisulfate, silver(II) oxide, and hydrogen peroxide in an alkaline, concentrated, aqueous sodium chlorate solution. Thus, the oxidation studies were limited to acid media.

Chlorates are decomposed by strong acids with the formation of perchlorates. In order to distinguish between the perchlorate formed due to the action of the acid alone from that produced by the oxidizing agent, experiments were done in which perchlorate yields were determined for acid decomposition alone under conditions identical with those used in the subsequent chemical oxidation experiments. In all chemical oxidation experiments 10 ml. of solution was used, and where the addition of sodium chlorate is indicated, the dry salt was added to 10 ml. of the acid solution. The

amount of perchlorate produced from the decomposition of chlorates with the appropriate acids, together with the experimental conditions are shown in Table 4.

Preliminary experiments were carried out in which perchlorate was determined qualitatively with methylene blue reagent. Essentially no perchlorate was produced over a period of 24 hours by the action on aqueous 4.5 M sodium chlorate, 1.5 M in sulfuric acid, of potassium peroxydisulfate alone or in conjunction with platinum(IV) oxide 4-hydrate, platinum(IV) oxide hydrate, platinum(powder), copper(II) sulfate, cerium(IV) oxide, and iron(III) oxide at 40 degrees C. In the absence of peroxydisulfate no perchlorate was produced when chlorate solution was treated with platinum(IV) oxide 4-hydrate, platinum(IV) oxide hydrate, potassium periodate, and sodium bismuthate. Perchlorate was produced with peroxydisulfate catalyzed by silver ions.

In many cases the effectiveness of oxidizing agents for the formation of perchlorate was determined quantitatively. Oxidizing agents were tested under three different sets of conditions: (a) with 10 ml. of 3 M chloric acid solution at 30 degrees C., (b) with 10 ml. of 3 M chloric acid solution at 65 degrees C., and (c) with a mixture of 47 millimoles of sodium chlorate and 10 ml. of 9 M sulfuric acid solution. Solutions were first brought to the indicated temperature and then the oxidizing agent was added slowly and with stirring. In experiments in which chlorate was used with 9 M sulfuric acid, the mixture was stirred for about an hour before addition of the oxidizing agent in order to dissolve as much of the sodium chlorate as possible. The perchlorate yields, together with conditions under which the experiments were carried out, are given in Table 5.

Of the oxidizing agents studied, lead(IV) oxide and potassium

TABLE 4

Yield of perchlorate from the decomposition of chlorates with acids.

Acid	NaClO ₃ added (millimoles)	Temperature (degrees C.)	Reaction time (hrs.)	Perchlorate yield (millimoles)
3 M HClO ₃	0	30	48	0
		65	24	(trace) ≤ 0.3
	47	30	48	0
9 M H ₂ SO ₄	47	30	48	1.8
15.6 M HNO ₃	47	30	48	2.3

TABLE 5

The efficiency of some oxidizing agents on oxidation of chlorate solutions to perchlorate. (A) 10 ml. 3 M HClO_3 ; temperature: 30 degrees C.; reaction time: 48 hours. (B) 10 ml. 3 M HClO_3 ; temperature: 65 degrees C.; reaction time: 24 hours. (C) 10 ml. 9 M H_2SO_4 to which 47 millimoles NaClO_3 were added; temperature: 30 degrees C.; reaction time: 48 hours.

Oxidizing agent	Conditions	Total oxidizing agent	Perchlorate yield (millimoles)	Perchlorate yield (percent of theoretical)
Ag_2O	A	12.1	0.6	10
	B	12.3	(trace)	3
	C	24.3	1.9	16
$\text{K}_2\text{S}_2\text{O}_8$ (0.15 M AgNO_3)	A	6.09	4.4	72
	B	6.07	1.9	31
	C	12.1	1.4	12*
Bi_2O_4	A	4.95	0	0
	B	4.96	0	0
	C	9.35	2.5	27
NaBiO_3	A	4.96	(trace)	<3
	B	4.97	0	0
	C	9.93	6.3	63
$\text{Ce}(\text{SO}_4)_2$	A	5.14	0	0
	B	5.14	0	0
	C	15.5	3.0	39
Co_2O_3	A	9.08	0	0
	B	9.07	0	0
	C	18.1	1.4	8*

TABLE 5
(continued)

Oxidising agent	Conditions	Total oxidizing agent	Perchlorate yield (millimoles)	Perchlorate yield (percent of theoretical)
CrO_3	A	7.01	0	0
	B	6.76	(trace)	3
$\text{K}_2\text{Cr}_2\text{O}_7$	C	4.62	1.8	13*
BaFeO_4	A	3.62	0.5	9
	B	3.61	(trace)	3
	C	6.95	(trace)	3
Ni_2O_3	A	5.22	0.4	8
	B	5.21	0.2	4
	C	10.3	5.1	49
PbO_2	A	6.46	0	0
	B	6.43	0	0
	C	12.7	9.0	71
Ta_2O_5	A	3.40	0	0
	B	3.39	0	0
	C	6.80	1.8	26*
$\text{UO}_4 \cdot 2 \text{H}_2\text{O}$	A	6.06	0	0
	B	6.09	0	0
	C	12.1	(trace)	3
V_2O_5	A	6.06	0	0
	B	6.12	0	0
	C	12.1	(trace)	3
$\text{Ag}(\text{C}_5\text{H}_5\text{N}_2)_2(\text{ClO}_4)_2$ **	A	2.43	0	0
	B	1.78	0.19	21

*Yield of perchlorate equal to, or less than, that produced by the acid in the absence of the oxidizing agent.

**Silver(II) α -dipyridyl perchlorate.

TABLE 7

Yield of perchlorate on oxidation of chlorate solutions with lead(IV) oxide, reaction time: 48-hours for reactions at 30 degrees C. and 24-hours for the reaction carried out at 65 degrees C.

PbO ₂ (millimoles)	Solution composition	Temperature	Perchlorate yield (millimoles)	Perchlorate yield (percent of theoretical)
6.71	3 M HClO ₃ 4.7 M NaClO ₃	30	0	0
6.70	3 M HClO ₃ 4.7 M NaClO ₃	65	0	0
6.30	1.5 M H ₂ SO ₄ 3 M NaClO ₃	30	0	0
12.6	15.6 M HNO ₃ 4.7 M NaClO ₃	30	10	79

In order to determine the effect of acid concentration and temperature on perchlorate formation in which an unstable oxide is used as oxidising agent, experiments were done in which perchlorate yields were determined after oxidation of chlorate solutions with silver(II) oxide. Three experiments were carried out in which the acid concentration was varied while the chlorate concentration was kept constant. A fourth experiment was done

under the same conditions as indicated in Table 5 under (C) with the exception that the temperature was maintained at 0 degrees C. instead of at 30 degrees C. The results of these experiments are shown in Table 8.

TABLE 8

Yields of perchlorate upon oxidation of chlorate solutions with silver(II) oxide, as a function of acid concentration and temperature; reaction time: 48-hours.

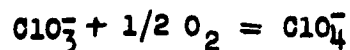
AgO (millimoles)	Solution composition	Temperature	Perchlorate yield (millimoles)	Perchlorate yield (percent of theoretical)
12.1	3 M NaClO ₃	30	0	0
12.1	2 M NaClO ₃			
	1 M HClO ₃	30	(trace)	< 3
12.1	1.5 M NaClO ₃			
	1.5 M HClO ₃	30	0.4	7
22.5	0	0	2.3	20

Experiments were done with silver(II) α,α' -dipyridyl chlorate upon the assumption that this compound may undergo self-oxidation with the formation of perchlorate. An aqueous solution of silver(II) α,α' -dipyridyl chlorate was prepared by replacing the nitric acid used in the preparation of the silver(II) nitrate complex⁴² with the equivalent amount of chloric

acid. The silver(II) ~~per~~ dipyridyl chlorate formed a deep red solution similar in color to that of the nitrate. The solution appeared to be stable at room temperature; however, when the solution was heated to 100 degrees C., the red color faded. Upon addition of sodium hydroxide to the solution, silver(I) oxide precipitated. Analysis of the clear supernatant liquid for perchlorate showed that only a trace of perchlorate was produced.

CONCLUSIONS

The oxidation of chlorate ions to perchlorate ions according to the equation



involves a negative free energy change of 8.75 kilocalories per mole.⁴⁸

From a thermodynamic point of view the oxidation should take place readily with a number of oxidizing agents. In actual practice it takes place only with a few strong oxidizing agents in acid media. In basic solutions, such strong oxidizing agents as peroxydisulfate, hypochlorite, silver(II) oxide and even electrolytic oxidation produce essentially no perchlorate.

In dilute acid solutions of chlorates (e.g. 3 M HClO_3) the only reagent which produced high perchlorate yields was peroxydisulfate in the presence of silver ions. In more concentrated acid solutions of chlorate (e.g. NaClO_3 in 9 M H_2SO_4) effective oxidizing agents were lead(IV) oxide, sodium bismuthate(V), and nickel(III) oxide, while some perchlorate was formed in cerium(IV) sulfate solutions.

Certain similarities may be seen between conditions favorable to electrolytic and to chemical oxidation of aqueous chlorates. In the electrolysis of chlorate solutions the highest yields of perchlorate are obtained in acid electrolytes and at low temperatures. In chemical oxidation experiments it was shown that the same factors which favor high perchlorate yields in the electrolytic process also resulted in high perchlorate

⁴⁸Free energy values were obtained from "Handbook of Chemistry and Physics", Thirty-first Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, O. D. Hodgman, Ed., p. 1538.

yields in chemical oxidation experiments. The effect of low temperature in favoring perchlorate formation was clearly demonstrated by the oxidation of 3 M chloric acid solution with peroxydisulfate in the presence of silver ions. At 30 degrees C. the yield was 72 percent while at 65 degrees C. under otherwise identical conditions, the yield was only 31 percent.

It is supposed that the mechanism for the electrolytic formation of perchlorates involves an unusually high valence oxide which forms on the anode surface. In the highly acid conditions existing at the anode surface the oxide is unstable and reacts similarly to higher oxides in chemical oxidation experiments. It is expected that anode materials with which an oxide of that type cannot be formed (e.g. gold and graphite) no perchlorate is formed. High current densities required for oxidation of chlorate solutions at lead(IV) oxide electrodes probably reflected the necessity for higher acid concentrations in those cases, which was provided by the greater concentration polarization and enhanced hydroxyl ion discharge. In the case of the platinum anode an oxide is formed on the surface which is less stable than that of lead and thus requires a lower acid concentration, just as in chemical oxidation experiments silver(II) oxide required a lower acid concentration to oxidize chlorate to perchlorate than did lead(IV) oxide.

Oxygen evolution at the platinum electrode has been attributed to the formation and decomposition of platinum(IV) oxide under anodic polarization conditions existing at that electrode⁴⁹. In chlorate solutions, increase of current density and electrode potential beyond that required

⁴⁹S. E. S. El Wakad and S. H. Emara, J. Chem. Soc. 461 (1952).

for oxygen evolution leads to increased oxidation of chlorate and relatively lower yields of gaseous oxygen. The observations may be explained most easily by proposing that an unstable platinum(VI) oxide is formed under those conditions which does not decompose to form oxygen in the presence of chlorate ions, but rather forms an intermediate with chlorate ions, which may re-dissociate, or alternatively break down into platinum(IV) oxide and perchlorate ions.

In acid solutions it is expected that platinum(VI) oxide does not form at high temperatures, and in basic solutions the relatively stable perplatinate(VI) is most likely to be formed instead of the oxide.⁵⁰ Those expectations are compatible with the experimental facts regarding chlorate oxidation at the platinum anode.

The postulate of a higher oxide intermediate circumvents certain difficulties inherent in earlier theories: (1) no peroxides are involved, and (2) active oxygen is not presumed to be the active oxidizing agent. Qualitative tests showed that no peroxides were formed at any time during electrolysis of simple chlorate solutions, nor did any of the peroxides used as oxidants lead to the formation of perchlorate, so that mechanisms based on peroxide species are implausible. Conditions which should lead to production of large amounts of "active oxygen" (e.g., anodic oxidation at a gold electrode) are not necessarily favorable to perchlorate formation. Furthermore, neither the active oxygen theory nor the peroxide theory explains satisfactorily the behavior of the system with respect to temperature.

⁵⁰L. Wohler and F. Martin, Ber. 42, 3326 (1909).

Cerium(IV) sulfate appears to be an anomaly. It should be remembered, however, that species in concentrated cerium(IV) sulfate solutions are quite complex and not well known, so that formation of perchlorate in such solutions cannot be used as evidence either for or against the mechanism proposed.

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