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NOTE TO USERS

PREPARATION OF PERBROMATES

by

Wesley F. DeCoursey

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

/In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1953

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I. INTRODUCTION

A. Statement of the Problem

The many and varied uses of periodates and perchlorates, and the rise in importance of these compounds due to their unique properties, makes the non-existence of perbromates a tantalizing problem for study. It is even more curious to find no sound theoretical reason why they should be non-existent.

In beginning chemistry, much is made over the similarities of elements in families, such as the alkalis or halogens. This is a helpful concept but must not be carried too far, as can be seen by comparing the formulas, properties, and uses of the perchlorates with the periodates. With bromine being in between chlorine and iodine, it would seem reasonable that the perbromates would be similar either to the perchlorates or the periodates.

An early statement by Robertson[1] that the interatomic vibrations are probably too strong for the molecule to hold together was based only on the fact that it, as yet, had not been prepared. It does not follow that a molecule is necessarily unstable simply because it has not yet been made.

Recently Hugus[2] proposed that 4 f orbitals were available to make enhanced stability of the higher oxidation states of iodine, antimony, and tellurium, but were not available for the formation of compounds such as

$AsCl_5$, $AsBr_5$, and $HBrO_4$; the non-existence of these compounds should not

be considered abnormal, but the enhanced stability of the compounds of the

elements in the second long period of the chart should be considered as

abnormal.

It might be that 4 f orbitals for iodine make it perfectly normal

for the formation of a coordination number of six, as in H_5IO_6; but the

lack of 4 f orbitals in bromine should not be regarded as evidence for the

lack of a coordination number of four for bromine in $HBrO_4$. Bromine can,

at least with fluorine, have a coordination number of five in BrF_5.

Pauling,[3] in a lecture on "Unsolved Problems of Structural Chemistry,"

refers to the problem of explaining the non-existence of perbromic acid

and states:

> It might be suggested that bromine lies just in the middle of
> the transition from a stable acid with a coordination number
> four, such as $HClO_4$, to a stable acid with coordination number
> six, such as paraperiodic acid, H_5IO_6. However, the existence
> of salts of periodic acid with coordination number four, such
> as KIO_4, renders this explanation unsatisfactory.

The stable structure and formula of an acid depends on ρ, the ratio

of cation radius to anion radius, according to Pauling.[4] A triangular

arrangement of atoms is favored when ρ is 0.225 or less, a tetrahedron

when ρ is 0.225 to 0.414, an octahedron when ρ is 0.414 to 0.713, and a

coordination number eight when ρ is over 0.713. ρ for chlorine is 0.28,

ρ for bromine is 0.35, and ρ for iodine is 0.44. Pauling states: "The

assumption from the data is that there is no apparent reason why BrO_4^-

should not also form and be the correct formula rather than bromine

forming acids similar to the periodates IO_6^{-5}."

It is often pointed out that in going down the halogen family of

elements the gradation of properties shows large deviations between chlorine and iodine, and that bromine is caught in between a coordination of four and six. This is true, but the reasons for bromine not forming a coordination number of four or six apparently remain unknown.

In attacking the problem, it was believed that if the oxidation potential needed to form perbromates were very high, then it would require some of the best oxidizing methods available.[5](p. 12) These methods are by fluorine, ozone, peroxydisulfate, 90% hydrogen peroxide, and anodic oxidation. If perbromates are more unstable than perchlorates or periodates, then oxidation at low temperatures should be tried; or if the perbromates are unstable in aqueous solutions, then oxidation in liquid ammonia or in organic solvents might be the answer.

The problem had not been worked on for a great many years and seemed worthy of an exhaustive study in light of modern techniques, such as the stabilization of oxidation states with isomorphous compounds of the same oxidation state,[5](p. 8) ozone in liquid ammonia,[6] fluorine gas,[7] catalysts with high oxidation potentials,[8] superoxides of the alkali metals, and oxidation in the anhydrous fused state.

The nature of perbromates being unknown suggested the procedure of using any or all possible methods known to be capable of forming perchlorates and periodates under conditions which seemed to offer possible success. These will be discussed further in subsequent portions of this thesis. The tests for the detection of perbromates being unknown suggested the procedure of using methods of analysis such as oxidizing power, spot tests, and precipitation tests used for perchlorates and periodates.

Table 1

Comparison of Oxidation Potentials

Acid Solution

$$F^- \xrightarrow{-2.87} F_2$$

$$Cl^- \xrightarrow{-1.36} Cl_2 \xrightarrow{-1.47} ClO_3^- \xrightarrow{-1.19} ClO_4^-$$

$$Br^- \xrightarrow{-1.07} Br_2 \xrightarrow{-1.52} BrO_3^- \xrightarrow{?} BrO_4^-$$

$$I^- \xrightarrow{-0.53} I_2 \xrightarrow{-1.20} IO_3^- \xrightarrow{-1.7} H_5IO_6$$

Basic Solution

$$F^- \xrightarrow{-2.85} F_2$$

$$Cl^- \xrightarrow{-1.36} Cl_2 \xrightarrow{-0.4} ClO^- \xrightarrow{-0.50} ClO_3^- \xrightarrow{-0.36} ClO_4^-$$

$$Br^- \xrightarrow{-1.07} Br_2 \xrightarrow{-0.45} BrO^- \xrightarrow{-0.54} BrO_3^- \xrightarrow{?} BrO_4^-$$

$$I^- \xrightarrow{-0.53} I_2 \xrightarrow{-0.45} IO^- \xrightarrow{-0.56} IO_3^- \xrightarrow{-0.7} H_5IO_6$$

Reaction	E^0 Volts
$F_2 + 2e \longrightarrow 2F^-$	2.87
$F_2 + 2e + 2H^+ \longrightarrow H_2F_2 \text{ aq}$	3.06
$OF_2 + 2e + 2H^+ \longrightarrow H_2O + 2F^-$	2.10
$O_3 + 2e + 2H^+ \longrightarrow O_2 + H_2O$	2.07
$Cl_2 + 2e \longrightarrow 2Cl^-$	1.36
$Br_2 + 2e \longrightarrow 2Br^-$	1.07
$I_2 + 2e \longrightarrow 2I^-$	0.53
$H_2O_2 + 2e + 2H^+ \longrightarrow 2H_2O$	1.77
$O_2 + 4e + 4H^+ \longrightarrow 2H_2O$	1.23
$S_2O_8^= + 2e \longrightarrow 2SO_4^=$	2.05
$AgO^+ + 2e + 2H^+ \longrightarrow Ag^+ + H_2O$	2.0
$Ag^{++} + e \longrightarrow Ag^+$	1.98
$Co^{+++} + e \longrightarrow Co^{++}$	1.84
$Bi^{+5} + 2e \longrightarrow Bi^{+3}$	1.70
$Mn^{+++} + e \longrightarrow Mn^{++}$	1.51

Table 1 gives some indication of the possible oxidation potential required for perbromate formation, and indicates the high oxidizing potential of elemental fluorine.[9] Even though the change of chlorate to perchlorate requires approximately a 1.2 volt potential, the most powerful chemical oxidants are necessary to bring about this change. This may be true for perbromates, also.

Table 2

Heats of Formation
of Some Halogen Acids and Potassium Halates[a]

Compound	H^f Kcal. per mole	Stability
HIO_3	-55	most stable
$HClO_3$	-23	less stable
$HBrO_3$	-9	least stable
H_5IO_6	-183	most stable
$HClO_4$	-31	less stable
$HBrO_4$	?	- - -
KIO_3	-115	most stable
$KClO_3$	-83	less stable
$KBrO_3$	-69	least stable
KIO_4	-97	most stable
$KClO_4$	-91	less stable
$KBrO_4$	?	- - -

[a]Values taken from U. S. National Bureau of Standards, "Selected Values of Chemical Thermodynamics," U. S. Dept. of Comm. Circular 500, Wash. D. C., U. S. Govt. Printing Off., 1952.

The heat of formation of a compound reflects the relative stability of that compound and especially its stability towards thermal decomposition. Table 2 shows clearly the reason for the assumption that perbromates may be less stable than the other perhalates.

B. Literature Survey

1. Perbromates

Kämmerar[10] originally reported perbromates and chlorine gas being formed when bromine reacted with perchloric acid. In 1876 MacIvor[11] reported that while a white precipitate was formed when a mixture of bromine and perchloric acid was neutralized with potassium hydroxide, this precipitate gave only potassium chloride upon being heated, thus proving that Kämmerar had not prepared potassium perbromate. MacIvor[12] also stated, in 1887, that Kämmerar's salts were probably perchlorates rather than perbromates. MacIvor heated perchlorates and bromine in sealed tubes but found no perbromates present. Muir,[13] in 1876, reported that he had repeatedly tried to prepare perbromates by Kämmerar's method and had failed; neither was he able to prepare perbromates by anodic oxidation. Wolfram,[14] in 1879, failed to confirm Kämmerar's work.

In 1894, Cook[15] reported that heating potassium iodate, potassium bromate, and potassium chlorate produced no periodates or perbromates whether the salts were partially or completely decomposed by heat.

In 1901, a further unsuccessful attempt to prepare perbromates was made by Michael and Conn[16] using perchloric acid, chloric acid, and

chlorine dioxide on bromine.

An effort to prepare perbromates by the same methods as perchlorates was made in 1912 by Robertson,[1] but no perbromates were obtained. His attempts included the oxidation of bromine with perchloric acid, periodic acid, and lead dioxide.

Allison[18,19] claims to have detected, with his magneto-optic method, the presence of the perbromate ion in solutions prepared by the Kämmerar method using perchloric acid and bromine.[17] The results obtained by this method have been questioned by other workers, even though the magneto-optic effect has been proved to exist by Hughes[20] and Bond,[21] and a review of the method has been made by Cooper and Ball.[22]

No other workers have reported any attempts to prepare perbromates by new methods since 1912, and the magneto-optic data are not considered to be specific enough or accurate enough to prove the existence of the perbromate ion.

2. Periodates

Numerous methods have been used to prepare periodates and are found in a number of well known inorganic texts.[23,24,25] Some of the chemical oxidizing agents used are ozone, fluorine, chlorine, bromine, potassium peroxydisulfate, and nitric acid.

Ammermuller and Magnus[26] discovered $Na_3H_2IO_6$ when they passed chlorine through an alkaline solution of sodium iodate. This method has been refined and described by Kimmins,[27] Lamb,[28] and Hill.[29] A similar method using bromine was reported by Lange and Paris.[30]

Anodic oxidation of iodates to periodates was accomplished with 100% current efficiency by Friedberger[31] and Müller[32] when they used PbO$_2$ anodes. Hickling and Richards[33] confirmed this but had low current efficiencies with Pt, graphite, and MnO$_2$ anodes. One of the most satisfactory methods of electrolytic oxidation of iodic acid has been described by Willard and Ralston.[34]

Although autoxidation occurs readily with some chlorates to give relatively good yields of perchlorates, only barium and sodium iodates give moderate yields of periodates when heated.

3. Perchlorates

Perchlorates have long been made commercially by anodic oxidation; and many procedures have been described in the literature, such as Bennett and Mack[35] who obtained a current efficiency of 95%. Mack[36] proposed the idea that in electrolysis ClO$_3$ is not liberated, but ClO$_3$⁻ simply adds an oxygen atom at the anode. To prove this, he undertook to prepare perchlorates by chemical oxidation under conditions where no ClO$_3$ could possibly be an intermediate, and from this to conclude that the mechanism which applied to the formation of perchlorates was the same by chemical means as by anodic oxidation. He obtained yields of 18% with sodium peroxydisulfate, 33% with sodium peroxydisulfate and the silver ion as a catalyst, and 1.8% with ozone. He also tried permanganic acid, hydrogen peroxide, sodium peroxide, and oxygen with ultraviolet light but failed to get appreciable amounts of perchlorates.

The beginning chemistry students often form perchlorates when heating

potassium chlorate to liberate oxygen. Mathers and Aldred[37] have obtained yields up to 55% by this method and report that added substances did not increase the yield.

Brown and co-workers[38,39] have done extensive work on the decomposition of potassium chlorate. Their work showed the effect of pressure and catalysts on the rate of chlorate decomposition.

In general, the perhalates may be formed by heating the halates; however, the mechanisms involved in this change are not well understood.

Perchlorates are much more difficult to form by chemical oxidation than periodates and more difficult than the oxidation potential would seem to indicate.

II. EXPERIMENTAL

A. Materials Used

The following list of materials includes those materials prepared by the author, those which deserve special mention, and those that were used often throughout the course of the work.

(1) Hydrogen Peroxide, H_2O_2: Becco Sales Corporation, Buffalo, N. Y. 90% H_2O_2.

(2) Fluorine, $F_2(g)$, $\frac{1}{2}$ lb. cylinder: Penn Salt Manufacturing Co., Philadelphia, Pa.

(3) Potassium Superoxide, KO_2: R. R. Miller, Naval Research Laboratories.

(4) Barium Superoxide, $Ba(O_2)_2$: Prepared by covering BaO_2 with 50 to 90% H_2O_2 for 36 hours, washing with alcohol and ether, and drying in a vacuum over anhydrone. 10-20% $Ba(O_2)_2$.

(5) Ammonium Bromate, NH_4BrO_3: Prepared by dissolving 15 grams of freshly precipitated $AgBrO_3$ in hot H_2O and precipitating the Ag^+ with the theoretical amount of NH_4Cl. Evaporation under a vacuum produces some crystals, but some care must be taken to keep the temperature below the decomposition temperature of the ammonium bromate.

(6) Silver Bromate, $AgBrO_3$: Prepared by precipitation from a solution of silver nitrate and sodium bromate.

(7) Silver Iodate, $AgIO_3$: Prepared by precipitation from a solution of silver nitrate and sodium iodate.

(8) Barium Bromate, $Ba(BrO_3)_2$: Prepared by precipitation from a solution of barium nitrate and sodium bromate, and dried under a vacuum.

(9) Barium Iodate, $Ba(IO_3)_2$: Prepared by precipitation from a solution of barium nitrate and sodium iodate, and dried under a vacuum.

(10) Cobalt Bromate, $Co(BrO_3)_2 \cdot 6H_2O$: Prepared by dissolving $AgBrO_3$ in hot water and precipitating the Ag^+ with $CoCl_2 \cdot 6H_2O$. The solution must be carefully dried under a vacuum and kept very cool, as the cobalt bromate decomposes readily. It decomposes below 100^0 C.

(11) Cobalt Chlorate, $Co(ClO_3)_2 \cdot 6H_2O$: Prepared by dissolving $Ba(ClO_3)_2 \cdot H_2O$ in water and precipitating the barium ion with $CoSO_4 \cdot 6H_2O$. The solution is evaporated over P_2O_5 under vacuum, and the cobalt chlorate is even more unstable toward heat than the bromate. Cobalt chlorate decomposes below 100^0 C.

(12) Ammonium Peroxydisulfate, $(NH_4)_2S_2O_8$: Becco Sales Corporation, Buffalo, N. Y. 85% $(NH_4)_2S_2O_8$.

(13) Potassium Bromate, $KBrO_3$: Baker and Adamson reagent grade.

(14) Sodium Bromate, $NaBrO_3$: Baker and Adamson reagent grade.

(15) Potassium Iodate, KIO_3: Baker and Adamson reagent grade.

(16) Sodium Iodate, $NaIO_3$: Baker and Adamson reagent grade.

(17) Potassium Chlorate, $KClO_3$: Baker and Adamson reagent grade.

(18) Sodium Chlorate, $NaClO_3$: Baker and Adamson reagent grade.

(19) Potassium Perchlorate, $KClO_4$: Baker and Adamson reagent grade.

(20) Sodium Perchlorate, $NaClO_4$: Baker and Adamson reagent grade.

(21) Potassium Periodate, KIO_4: Fisher Scientific Co. A. C. S. quality.

(22) Silver Nitrate, $AgNO_3$: Merck and Co., Inc., Rahway, N. J. Merck

    reagent grade.

B. Methods of Analysis

The methods for the detection and determination of perbromates are, of course, unknown; and the search for possible methods was one of the most difficult parts of the present work. The likelihood that similarities would exist between perbromates and periodates or perchlorates was considered to be the main possibility for the detection of perbromates. Various qualitative and quantitative tests for the halide, halate, and perhalate ions were selected from a number of sources.[40,41,42,43] These methods were used whenever conditions and interfering ions made them possible and applicable.

1. Oxidizing power

Oxidizing power is one of the principal properties used for the analysis of ions, such as bromate, iodate, and periodate. In the buffered solution of sodium bicarbonate and potassium iodide, the periodate will liberate iodine which is then titrated with 0.1 N arsenite solution. The bromate ion may be reduced with excess standard arsenite in a sodium bicarbonate buffered solution, and the excess arsenite titrated with 0.1 N iodine solution. Either the bromate or iodate can be determined by adding potassium iodide and hydrochloric acid, and then titrating the liberated

iodine with 0.1 N sodium thiosulfate. In the absence of oxidizing agents such as ozone, hydrogen peroxide, and fluorine, the ability of the periodate ion to liberate iodine from an alkaline solution of potassium iodide is used as a qualitative test for the periodate ion. This same test was used as a possible test for the perbromate ion in instances where oxidizing agents and the periodate ion were known to be absent. The bromate ion may be detected by its rapid decolorizing of methyl orange in hydrochloric acid solutions, or by its liberation of bromine from potassium bromide in cold dilute sulfuric acid. Some solutions and precipitates, which contained no oxidizing agents but the bromate, were analyzed for total oxidizing power with the assumption that if perbromates had been formed during the reaction there would be more oxidizing power present than the calculated amount for the bromate alone.

2. **The halides**

The detection and determination of the chloride, chlorate, perchlorate, and bromide ions usually involved their reduction to the halide and their titration with 0.1 N silver nitrate. The end point was determined with a sodium chromate or dichlorofluorescein indicator.

The solutions of chloride, chlorate, and perchlorate were divided into three parts for analysis. One part was titrated directly with 0.1 N silver nitrate for the chloride content. A second part was treated with sulfur dioxide to reduce the chlorate to chloride, and then titrated with 0.1 N silver nitrate. The perchlorate and chlorate were reduced in a third portion by a method used by Fowler and Grant.[45] This method was to

evaporate the solution to dryness in a platinum crucible and fuse the residue with two to three grams of sodium carbonate. The fused residue was then dissolved with dilute nitric acid, and the total chloride was determined by titrating with 0.1 N silver nitrate. This method was rapid and was used for some of the mixtures of bromide and bromate which might have contained some perbromate. The method can be used for the detection of perchlorates as well as their determination. Chloride-free sodium carbonate was used so that a blank was not necessary, although a check was occasionally made on the sodium carbonate.

The iodide ion was detected by the blue color imparted to a starch indicator solution when it was oxidized to free iodine.

3. Spot tests

A number of spot tests were used in attempting to detect the perbromate ion. Most of these tests were applicable to the perchlorate and periodate ions. The tests were used whenever the conditions appeared to give any hope of detecting the perbromate ion. It was hoped that a reagent would be found which might react toward the configuration of the ion rather than the composition of the ion.

a. A 1% methylene blue solution gives characteristic pink precipitates with ClO_4^- and $S_2O_8^=$. ClO_3^- gives blue to red dichroic prisms, and I^- produces fine purple crystals. The reagent can be used for the detection and determination of a number of other ions. Its reaction to these ions depends on three processes: (1) reducing substances convert the blue compound to a colorless leuco derivative, (2) oxidizing substances restore

the color to the leuco derivative, and (3) neutral salts form characteristic compounds with methylene blue.

b. A copper sulfate solution in pyridine, known as Zwikker's reagent, gives distinctive crystals with perchlorate, peroxydisulfate, chromate, and dichromate ions.

c. A solution of manganous sulfate in 85% phosphoric acid gives a purple color with the periodate and peroxydisulfate ions in the cold and with chlorate ions when heated. The solution liberates bromine from bromates. Oxidation of the manganese appears to be the main reaction with this reagent.

d. A brucine sulfate solution gives an orange color with the nitrate and persulfate ions and characteristic crystals with perchlorates.

e. Nitron forms insoluble precipitates with the nitrate, perchlorate, and a number of other ions. It can detect the iodide, chlorate, and bromide ions in glacial acetic acid.

f. A solution of 5-nitro-1, 10 phenanthroline ferrous sulfate gives precipitates with the perchlorate and periodate ions in the presence of moderate amounts of chlorates and iodates.

g. Tetraphenylarsonium chloride forms precipitates with the persulfate, perchlorate, periodate, and a number of other ions.

h. Benzidine in sulfuric acid gives an orange color with the chlorate, iodate, and nitrate ions. Benzidine in acetic acid gives a blue color with the persulfate ion, and benzidine alone produces a red-brown color with the perchlorate ion.

i. Morphine and strychnine solutions give characteristic crystals with the perchlorate ion. Strychnine in nitric acid solutions gives a

red color with the bromate and chlorate ions but not with iodates and perchlorates.

j. The solubility of the silver salts and other common salts was often a possible test for the presence of the ions.

4. Techniques

It was expected that small yields of the perhalates would be formed; and, because of the uncertainty of detecting the perbromate ion, a large number of the above tests and methods of analysis were made on the residues, precipitates, and solutions obtained in the experiments.

A polarizing microscope was used in many instances when making the spot tests using the organic precipitants. Known mixtures containing the ions were compared with the substance being tested in order to detect the presence of a new ion, the perbromate ion. Occasionally polarized light could be used to an advantage, as in the case of the oxidation of isotropic sodium bromate with ozone or fluorine. Sodium fluoride is also isotropic, and so the residues were examined for the presence of an anisotropic substance. It is highly probable that the compound, sodium perbromate, would be anisotropic.

C. Thermal Autoxidation

1. General considerations

The well known method, of heating a halate which then undergoes autoxidation and forms a halide and a perhalate, has been tried a number of

times to form all the perhalates. Cook[44] heated the potassium halates but obtained only the perchlorate. However, when the barium or sodium iodates are heated periodates are formed.[39] Fowler and Grant[45] found that heating sodium chlorate with silver oxide gave nearly 100% conversion to sodium perchlorate. They also obtained potassium perchlorate by heating lead dioxide with potassium chlorate. The reduction products were free silver and Pb_3O_4. Robertson[46] unsuccessfully attempted to prepare perbromates in the same way.

Recently Glasner and Weidenfeld[47] have worked on the problem of the mechanism of the decomposition of potassium chlorate by heat. They state that the usual explanation is given by equations (1) and (2).

$$KClO_3 \longrightarrow KCl + 3O \qquad (1)$$

$$4KClO_3 \longrightarrow 3KClO_4 + KCl \qquad (2)$$

These take place at the same time and account for the formation of potassium perchlorate as well as the liberation of oxygen. Glasner and Weidenfeld concluded that equation (2) was not the correct explanation, and that the formation of perchlorate was due to the addition of atomic oxygen to the chloride.

$$KCl + 4O \longrightarrow KClO_4 \qquad (3)$$

The decomposition of potassium perchlorate first formed the chlorate, and this in turn decomposed to the chloride.

$$KClO_4 \longrightarrow KClO_3 + O \qquad (4)$$

Since the formation of perbromates by heating would probably follow the same mechanism as the formation of perchlorates, it would be advantageous to know just what the mechanism is. A reasonable reaction, not mentioned by Glasner and Weidenfeld, is the formation of perchlorate by

the addition of atomic oxygen to the chlorate.

$$KClO_3 + O \rightleftharpoons KClO_4 \qquad (5)$$

This would take place as atomic oxygen became available from equation (1), or any other source of atomic oxygen. This would also explain the high yield of perchlorates obtained by Fowler and Grant,[45] whose source of atomic oxygen was presumably the decomposition of silver oxide and lead dioxide.

In order to further elucidate the reaction mechanism, potassium chlorate was heated with sodium bromate at a temperature that would decompose the bromate but not the chlorate. The result was a 98% conversion of chlorate to perchlorate, which would seem to suggest that equation (5) is a possible mechanism for the formation of potassium perchlorate and, in like manner, the perbromates. Equation (5) should therefore be written as a reversible reaction.

Zintl and Morawitz[46] have obtained high yields of sodium paraperiodate by heating sodium iodide and sodium hydroxide in air. Glasner and Weidenfeld[47] have shown that some potassium iodate and potassium bromate is formed when potassium perchlorate is heated with the iodide and bromide. Thus the following reversible reactions can be considered as possible:

$$NaI + 3O \rightleftharpoons NaIO_3 \qquad (6)$$

$$KI + 3O \rightleftharpoons KIO_3 \qquad (7)$$

$$KBr + 3O \rightleftharpoons KBrO_3 \qquad (8)$$

The preparation of perbromates was attempted by heating the bromate with compounds which would easily decompose and furnish atomic oxygen at a lower temperature than that at which bromates decompose.

2. Apparatus used

The apparatus available for controlled heating of solids was an auto-
matic recording balance[49] attached to a vertical heating oven. The oven
temperature was maintained by a thermocouple and potentiometer, while the
voltage input was regulated by a thermostat and relay regulator. Temper-
ature fluctuations were controllable to 3^0 or 4^0 even over periods of two
days or more. The glass sample tube was suspended on a balance which con-
tinuously weighed the sample. An electronic control unit relayed the
weight change to an automatic recorder by way of a light beam and a photo-
cell. The graphs produced by the recorder show the rate of oxygen loss
from the substances heated. The changes in weight were recorded with an
accuracy of 0.5%, and a change in weight of ten mg. would cause a fluctu-
ation of over an inch on the recording paper. This apparatus is extremely
useful and accurate for the continuous recording of small weight changes
at nearly constant temperature.

3. Data and results

Curve "c" in Figure 1 shows the rate of loss of oxygen from one gram
of pure potassium bromate at 350^0. This sample was heated for 50 hours
and lost only 28% of its oxygen content. Curve "b" in Figure 1 shows the
influence of 1% manganese dioxide catalyst. These curves are very similar
to potassium chlorate decomposition curves run on the same apparatus and
in the same way. Curve "a" in Figure 1 is the rate of loss of oxygen from
one gram of potassium bromate at 360^0 with 1% manganese dioxide catalyst,
showing the effect of a rise in temperature on the loss of oxygen rate.
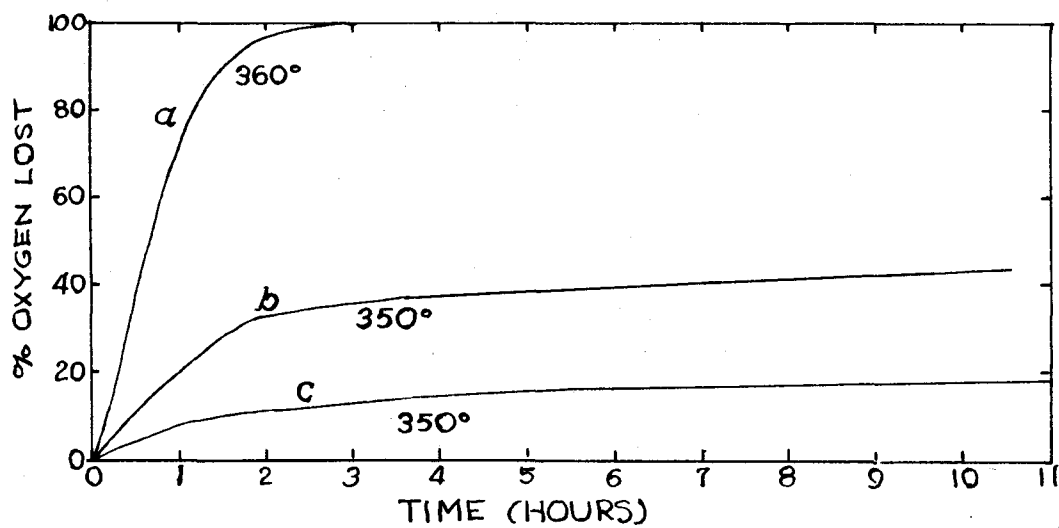
FIGURE 1. DECOMPOSITION OF POTASSIUM BROMATE
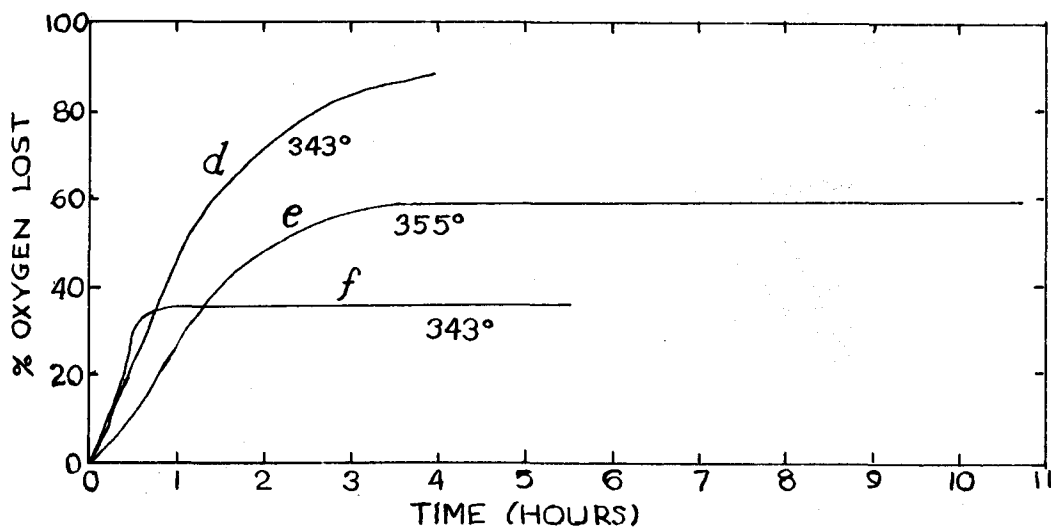
FIGURE 2. DECOMPOSITION OF SODIUM BROMATE AND MIXTURES

Curve "d" in Figure 2 represents the loss of oxygen rate from 0.5 gram of sodium bromate at 343^0. Curve "e" in Figure 2 shows the change produced when 0.5 gram of potassium chlorate is mixed with 0.5 gram of sodium bromate and heated at 355^0. Curve "f" in Figure 2 represents the rate of loss of oxygen from 0.5 gram of sodium bromate mixed with one gram of potassium chlorate at 343^0.

There are several features of the curves in Figures 1 and 2 that should be mentioned: first, the curves are not first order decomposition curves; and, at slow rates of decomposition like "b" and "c", the loss of oxygen practically ceases before even 50% of the oxygen is lost. Second, the addition of potassium chlorate, shown by curves "e" and "f", decreased the amount of oxygen lost. The analyses showed that with more potassium chlorate present less oxygen was lost, and that the oxygen was taken up by the potassium chlorate to form potassium perchlorate. With equal amounts of bromate and chlorate, shown by curve "e", 60% of the oxygen from the bromate was lost while the other 40% was taken up by the chlorate to give a 98% yield of perchlorate. The ratio of two parts chlorate to one part bromate resulted in a loss of only 36% of the bromate oxygen - 64% was taken up by the chlorate. Third, higher temperatures, as well as the manganese dioxide catalyst, increased the rate of the loss of oxygen.

Barium iodate can be heated to give barium periodate; therefore barium bromate was prepared, dried, and heated in an attempt to obtain barium perbromate. The rate of loss of oxygen is shown for a temperature of 343^0 in curve "g" of Figure 3. All the oxygen was lost in less than an hour at this temperature; but at a temperature of 260^0, shown in
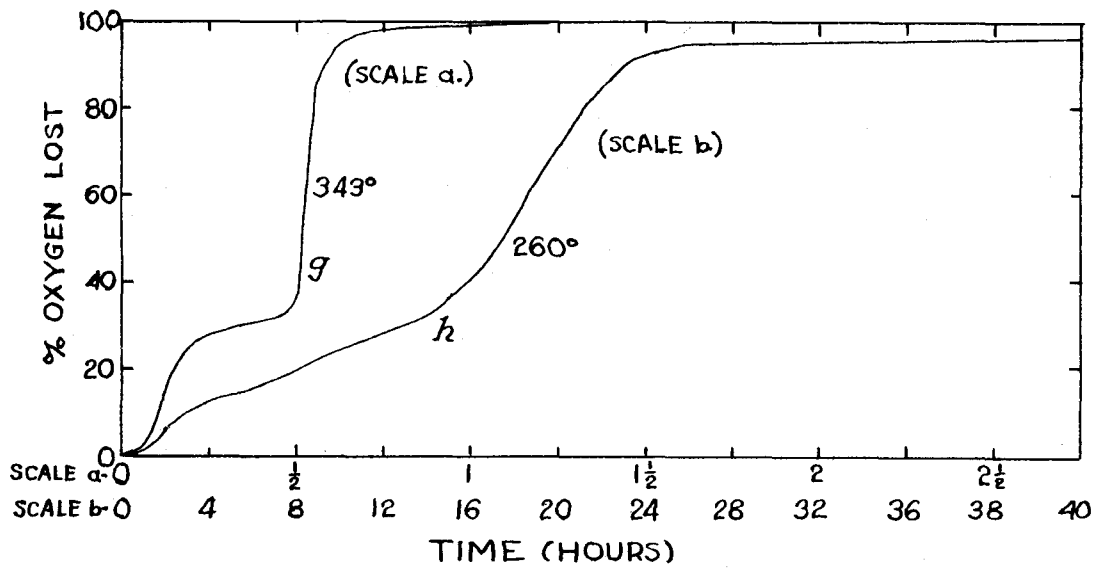
FIGURE 3. DECOMPOSITION OF BARIUM BROMATE
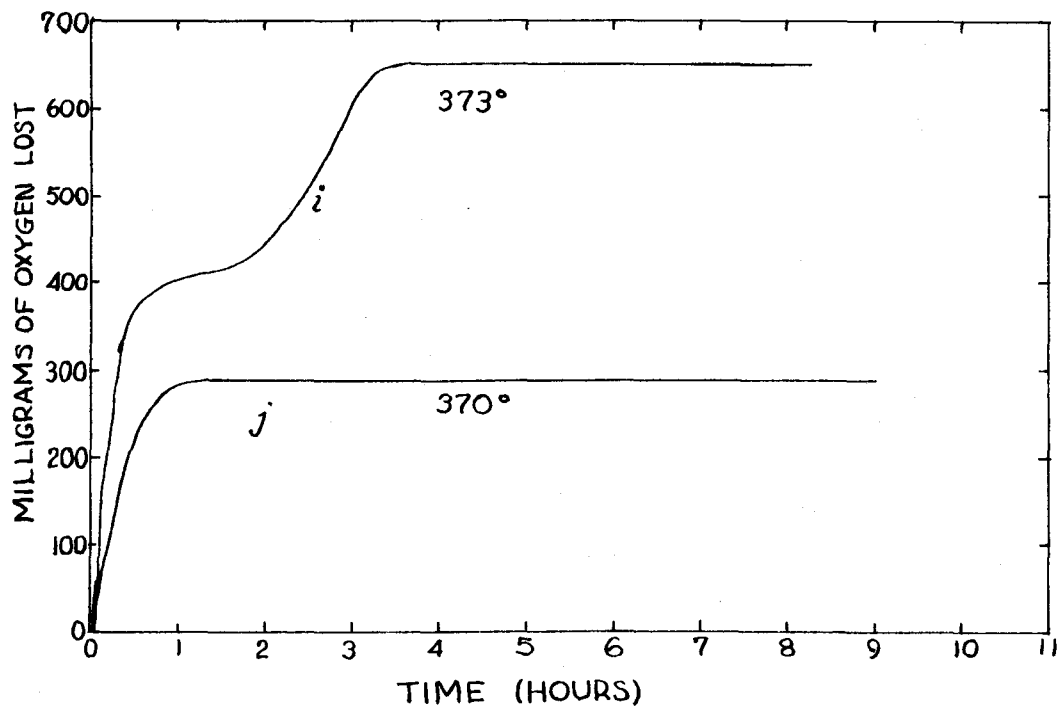
FIGURE 4. DECOMPOSITION OF POTASSIUM BROMATE
AND POTASSIUM PERCHLORATE MIXTURES

curve "h", all the oxygen was lost only after 24 hours. Three samples
were heated at 260^0 and analyzed for perbromates: (1) after the very
unusual hour-long induction period, (2) after 8 hours, and (3) after 50
hours. Similar decomposition behavior has been noted by Potilitzin.[50]
No evidence was found for the presence of any perbromates in any of the
three samples.

Potassium perchlorate was heated with potassium bromate at 370^0 in
the hope that the presence of an isomorphous compound having the desired
oxidation state might stabilize the formation of the perbromate ion. This
type of thing has been reported by Kleinberg.[5](p. 9) Curve "j", in Figure
4, is the rate of loss of oxygen for this experiment. Curve "i" is the
rate of loss of oxygen for a mixture of potassium perchlorate, potassium
bromate, and sodium nitrate heated to 373^0. The sodium nitrate was added
to lower the melting point of the mixture so that the fused state might
aid in atomic oxygen being taken up by the bromate ion. This curve "i"
seems to indicate the decomposition of both the bromate and perchlorate
almost completely, even though the temperature is far below the decomposi-
tion temperature for the perchlorate. The analysis of the residue showed
the presence of a trace of perchlorate, a little chlorate, and no bromate
or evidence of perbromate. The apparent decomposition of the bromate be-
fore the perchlorate is unexplained. Even though the potassium bromide
formed might catalyze the decomposition of the perchlorate, a smooth curve
would have resulted instead of the definite break in the curve. This
break coincides with the maximum available bromate oxygen.

Sodium bromate was heated with a sample of potassium chloride that

had been obtained by completely decomposing potassium perchlorate by heat. This experiment was carried out at 343° with the expectation of forming some potassium perchlorate. This should take place, according to the conclusions of Glasner and Weidenfeld;[47] however, no chlorate or perchlorate was present in the residue. This would indicate that, of the following reactions, (9) is the easiest to bring about under the conditions of the experiments.

$$KClO_3 + O \longrightarrow KClO_4 \qquad (9)$$

$$KCl + 3O \longrightarrow KClO_3 \qquad (10)$$

$$KCl + 4O \longrightarrow KClO_4 \qquad (11)$$

Table 3

The Decomposition of Mixtures of Sodium Bromate and Potassium Chlorate

Substance	Temp.	Time	Oxygen lost	$KClO_3$ changed to $KClO_4$	$NaBrO_3$ decomposed
1/2 g. $NaBrO_3$ 1/2 g. $KClO_3$	343°	10 hrs.	59.5%	98.5%	98.5%
2/3 g. $NaBrO_3$ 4/3 g. $KClO_3$	343°	6 hrs.	36%	77.5%	99%
1/3 g. $NaBrO_3$ 2/3 g. $KClO_3$	265°	5 hrs.	47.7%	19.2%	22.6%
1/3 g. $NaBrO_3$ 2/3 g. $KClO_3$	235°	46 hrs.	55%	32%	52%

4. Related experiments

Sodium nitrate was used in several experiments to lower the fusion
point of the mixtures, in order to obtain a more intimate contact between
bromate ions and atomic oxygen.

Some preliminary attempts to prepare perbromates were carried out by
heating solid bromates mixed with various oxidizing agents. These mix-
tures were placed in porcelain boats in a pyrex tube and heated while pas-
sing a stream of ozonized oxygen over the samples. The ozone would prob-
ably have no effect whatever, since its decomposition by heat would likely
take place before it came in contact with the sample. Data for these ex-
periments are listed in Table 4.

An oxidizing agent was sought which would decompose at a lower tem-
perature than the bromates and permit the bromate to take up atomic oxy-
gen. Oxidizing agents tried with bromates were: silver, lead, and mercu-
ric oxide; barium, sodium, and potassium peroxides; barium bromate; potas-
sium permanganate; ammonium and potassium peroxydisulfates. No evidence
of perbromates was found, and most of the oxidizing agents decomposed too
easily or catalyzed the decomposition of the bromate.

5. Discussion of results

The data plotted in Figures 1 and 2, and the data listed in Table 3,
clearly indicate the ability of the chlorate to take up atomic oxygen at
a relatively low temperature. They also indicate the possibility of pro-
ducing 100% yields of perchlorates by using excess bromate, or the possi-
bility of utilizing most of the bromate oxygen by using excess chlorate

Table 4

Oxidation of Halates with Metal Peroxides and Superoxides

Substance	Oxidizing agent	Results
$KClO_3$	K_2O_2	some ClO_4^- formed
$NaClO_3$	Na_2O_2	some ClO_4^- formed
$NaClO_3$	$Ba(O_2)_2$	some ClO_4^- formed
$KClO_3$	KO_2	some ClO_4^- formed
$KBrO_3$	KO_2	decomposed to Br^-
$KBrO_3$ $KClO_3$ }	--	some Br^-, Cl^-, and ClO_4^- formed
$NaIO_3$	$Ba(O_2)_2$	some IO_4^- formed
$NaIO_3$ $NaBrO_8$ }	$Ba(O_2)_2$	some Br_2 and I_2 liberated no IO_4^- or BrO_4^- formed
$Ba(BrO_3)_2$	$Ba(O_2)_2$	no BrO_4^- formed
$NaBrO_3$	Na_2O_2	decomposed to Br^-
$KBrO_3$	Ag_2O	decomposed to Br^-
KIO_3	Ag_2O	decomposed to I^-
$KClO_3$	Ag_2O	some ClO_4^- formed

at the proper temperature.

Work done by Glasner and Weidenfeld[47] showed the presence of potassium iodate and bromate in the residues after heating mixtures of potassium iodide with potassium perchlorate, and mixtures of potassium bromide with potassium perchlorate. They also found chlorate in residues of partially decomposed perchlorate. From these data, and data from experiments listed in Table 3, it seems reasonable that the following reactions can take place:

$$KIO_3 \rightleftharpoons KI + 3O \tag{12}$$

$$KBrO_3 \rightleftharpoons KBr + 3O \tag{13}$$

$$KClO_3 \rightleftharpoons KCl + 3O \tag{14}$$

$$KClO_4 \rightleftharpoons KClO_3 + O \tag{15}$$

They can be caused to go in either the forward direction or the reverse direction, depending upon conditions. It is assumed that the formation of halates would take place readily if the halides could be furnished abundant atomic oxygen at the proper temperature.

It was concluded that the bromate might accept atomic oxygen at a temperature below its decomposition temperature and thus form the perbromate. A large number of substances were tried; no positive results were obtained.

The curves in Figure 3 for the decomposition of barium bromate show a relatively long induction period. There is a period of one hour at 260°, during which time no loss of oxygen occurs. It was thought that barium perbromate might be forming during this time, so an analysis was made on a sample at the end of one hour; but no bromide was present in the sample.

The unusual flat portion of the curves seemed to indicate the existence of some equilibrium, possibly between perbromate, bromide, and bromate. A sample was analyzed after 8 hours of heating at 260^0; but the bromide content, bromate content, and loss of oxygen gave no indication of perbromates. No explanation could be found for the unusual behavior of this compound as shown on the graph in Figure 3.

Curves "b" and "c", of Figure 1, illustrate the type of curve obtained when potassium chlorate is heated at temperatures somewhat below its normal decomposition temperature. In curves "b" and "c" the loss of oxygen almost ceases after an initial relatively rapid rate of decomposition. Glasner and Weidenfeld,[47] in reference to potassium chlorate decomposition, interpret this as an equilibrium involving potassium chloride and perchlorate.

Because no perbromate was found to be present in any of the experiments in heating bromates, it was believed that an equilibrium between the bromate, bromide, and atomic oxygen as given in equation (13) might produce this same type of curve. A slow loss of oxygen continues, since whenever atomic oxygen forms molecular oxygen it is lost from the mixture.

A reaction of potassium bromate and atomic oxygen might be possible and might actually take place as potassium bromate is decomposed by heat. If the perbromate is less stable than the bromate, then there would be very little perbromate present in the mixture at any given instant. However, the perbromate might be formed if the bromate could be furnished an outside source of atomic oxygen at a lower temperature. These experiments did not accomplish this; however, only a small amount of time was spent on

this phase of the work. More work should be done in trying to obtain compounds that would liberate atomic oxygen easily while not catalyzing the bromate decomposition. Metal bromates with high decomposition temperatures should be heated with metal bromates with low decomposition temperatures. Alkali chlorates that decompose at a lower temperature than that of certain alkali bromates might offer a good chance of success in forming the perbromate.

D. Ozone Oxidation

1. General considerations

Ozone can be produced easily in an ozonizer but only in low concentrations; and, being a gas, it does not lend itself well for intimate contact with the substance being oxidized. Nevertheless, its oxidation potential[51] (2.07 volts) is one of the highest, being lower only than fluorine and atomic oxygen. It is easy to handle, does not introduce impurities, and can be removed readily from solutions by bubbling air through the solution for a short time. Willard and Merritt[52] point out, in summarizing its analytical applications, that most elements are oxidized to their highest oxidation states by prolonged action of ozone. The manganous ion is oxidized to permanganate, the chloride ion to perchlorate, the iodide ion to periodate, and the bromide ion to bromate. Other workers have reported similar results - such as ozone and moist chlorine forming perchloric acid, and bromine and ozone forming Br_3O_8.

2. Apparatus used

The source of ozone used in these experiments was a conventional, commercial, silent electrical discharge type ozonizer. The main features were a copper coated glass tube 6 x 24 inches sealed in a metal jacket and a rheostat which controlled the silent electrical discharge. Oxygen was passed through the tube at rates of from 5 to 50 liters per hour, and the ozone produced varied between 6 and 1 per cent ozone as measured by liberating iodine from potassium iodide and titrating with thiosulfate.

The ozone was dried with anhydrous magnesium perchlorate, conducted to the reaction vessels through plastic tubing, and bubbled into the solutions through a glass tube with small openings to increase the number of ozone bubbles. However, large holes were necessary in many instances due to the clogging of the small holes with newly-formed products of the reaction.

Dry ice and acetone cooling baths in vacuum bottles were used for the experiments carried out with ozone in liquid ammonia.

3. Experiments in non-aqueous solvents

The possibility that the perbromate ion is unstable in aqueous solutions suggested the possibility of being able to form it in organic solvents or liquid ammonia in which it might be stable. Also, the low temperature of liquid ammonia would further increase the possibility of holding the compound, once formed, if it were unstable at room temperatures. This is true for certain ozonates and superoxides formed in liquid ammonia with ozone, as reported by Whaley and Kleinberg.[53]

Table 5

Ozone Oxidation of Halates in Organic Solvents

Substance	Weight	Solvent
$NaBrO_3$[a]	not weighed	ethyl acetate
$NaBrO_3$[a]	0.3181	acetone
$NaBrO_3$[a]	0.3064	t-amyl alcohol
$NaBrO_3$[a]	0.2960	dioxane
$NaBrO_3$[a]	0.5182	anhydrous methyl alcohol
$NaBrO_3$	0.2884	absolute ethanol
$NaBrO_3$	0.5403	glacial acetic acid
$NaClO_3$	0.3298	ethyl acetate
$NaClO_3$	0.3071	acetone
$NaClO_3$[a]	0.2911	anhydrous methyl alcohol
$NaClO_3$[a]	0.3462	absolute ethanol
$NaClO_3$	not weighed	pentanol
$NaIO_3$[a]	0.3615	ethyl acetate
$NaIO_3$	0.1514	acetone
$NaIO_3$[a]	0.2910	anhydrous methanol
$NaIO_3$	0.3030	absolute ethanol
$NaIO_3$	not weighed	toluene

[a]Experiments repeated with potassium salts gave similar
results.

Table 5 summarizes some typical experiments with organic solvents used and the results obtained. The samples and reaction flask were weighed before treatment with ozone and again after the solvent had been evaporated off. A gain in weight would be indicative of any extensive addition of oxygen. Spot tests and qualitative tests were used where possible. The low solubility of the salts in most organic solvents is a major difficulty in obtaining results in this manner. The length of time allowed for the ozone treatment was from one to ten hours with an average of two hours.

In all cases the gain or loss in weight was so small that it could not be considered of importance; and the qualitative tests substantiated this, since no trace of periodates or perchlorates were found by this procedure. However, several later experiments using traces of moisture or pellets of potassium hydroxide in methanol, ethyl acetate, and acetone gave traces of periodates after treatment with ozone.

Ozone bubbled into liquid ammonia gives an orange color which disappears upon warming and evaporation of the ammonia.[54] Manchot[7] reported a deepening of the orange color when a small amount of moisture was present but a disappearance upon adding more water. He also found some oxidation products such as hydroxylamine, nitrites, and nitrates as residues from ozone and ammonia reactions. Both the orange color and oxidation products were found in the subsequent experiments.

Because of the small solubility of halates in liquid ammonia, finely ground halates were suspended in liquid ammonia and ozone bubbled through the suspension. Table 6 contains the data and results of a number of

Table 6

Ozone Oxidation of Halates in Liquid Ammonia

Substance	Wt. of sample	Time (hrs.)	Remarks[a]	Analysis
Br_2	1 ml.	0.5	white fumes and yellow ppt.	100% Br^-
KBr	0.5 gm.	1	orange color	100% Br^-
KCl	0.5 gm.	1	orange color	100% Br^-
KI	0.5 gm.	1	black ppt. of I_2	I_2 and I^-
$KClO_3$[b]	1.0 gm.	1.5	orange color	no ClO_4^-
KIO_3[b]	1.0 gm.	1.5	orange color	no IO_4^-
$KBrO_3$[b]	1.0 gm.	1.5	orange color	no BrO_4^-
NH_4BrO_3	- -	0.5	partially decomposed	Br^- and BrO_3^-
$NaBrO_3$	1.0 gm.	1	$NaNH_2$ added - orange color	100% BrO_3^-
$AgIO_3$	0.5 gm.	1	orange changing to brown	100% IO_3^-
$AgIO_3$	1.0 gm.	4	brown solution	100% IO_3^-
$AgBrO_3$	0.5 gm.	1	deep orange and tan ppt.	100% BrO_3^-
$AgBrO_3$	1.0 gm.	4	deep orange and tan ppt.	100% BrO_3^-

[a]All residues were white after evaporation of ammonia.

[b]Similar results were obtained using sodium salts.

these experiments. Silver halates were prepared and used because of their increased solubility in liquid ammonia. Some unusual color changes were noticed which were probably caused by the action of light or perhaps were due to the formation of some silver compounds of higher valences.

Ammonium bromate was prepared with much difficulty due to its instability. It was expected to be more soluble in liquid ammonia than the alkali halates. Only moist impure crystals of the compound could be prepared and these did not give any satisfactory results.

No significant changes occurred while using liquid ammonia, probably due to the low solubility of salts and cold temperatures involved. The orange color present in most of the reactions was apparently due to the ozone and ammonia, and not to the substances being oxidized. Iodine was liberated from potassium iodide in liquid ammonia, but neither potassium bromide nor potassium chloride were changed. The silver halates were moderately soluble in liquid ammonia, and a color change indicated a reaction taking place. This probably was due to the oxidation of the silver ion. The resulting residues were practically white, and the original color always appeared upon warming or removal of the source of ozone. Analysis with qualitative tests under the microscope, as well as the titration of liberated iodine with thiosulfate, gave indications of only bromates and iodates.

In one experiment sodamide was added to the liquid ammonia to produce a basic solution, in the sense of ammonia as the solvent, in which the reaction could take place.

4. Experiments in aqueous solvents

It has long been known that ozone would oxidize iodates to periodates in water solution and, to a lesser degree, oxidize chlorates to perchlorates. This was found to be the case in the experiments carried out in this work, and the data and results are listed in Table 7. Only small amounts of perchlorates were obtained either in acid or basic solutions. Perchlorates tend to be more easily formed in acid solutions; and, in general, oxidation potentials for oxidizing agents are higher in acid solutions; but because bromates are so unstable in strong acids, only a few experiments were tried in acid solutions.

Periodates are quantitatively formed[52] in alkali metal hydroxide solutions, and good yields were obtained in these experiments. Longer runs gave higher yields, and in the one case of 0.5 gram sodium iodate with 5.0 grams of sodium bromate all the iodate was oxidized in eight hours. No excess oxidizing power was present over the theoretical amount for sodium bromate and tertiary sodium paraperiodate. The solution was analyzed by diluting and using aliquot portions. Spot tests and microscopic examination of the residues gave no evidence of any perbromate being formed. Residues were obtained by evaporation, neutralization with acetic acid and evaporation, and precipitation with alcohol.

The formation of tertiary sodium paraperiodate in the presence of the bromate ion was carried out in the hope that the oxidation state of seven for iodine would help stabilize a compound with the formula of $Na_3H_2BrO_6$.

The oxidation potential is higher in acid solutions, and perbromates

Table 7

Ozone Oxidation of Halogens and Halates in Aqueous Solvents

Sub-stance	Solvent	Time (hrs.)	Remarks	Analysis
$NaClO_3$[a]	H_2O	1.5	- - -	trace, ClO_4^-
$NaClO_3$[a]	0.1 N NaOH	3	90°	small amt. ClO_4^-
$KClO_3$	3 N KOH	2	60°	100% ClO_3^-
I_2	3 N KOH	5	90°	94% IO_3^-, 6% IO_4^-
Br_2	3 N KOH	4.5	90°	Br^-, BrO^-, 30% BrO_3^-
Br_2	0.1 N KOH	3	25°	Br^-, BrO^-, BrO_3^-
Br_2	conc. NaOH	2	25°	Br^-, BrO^-, BrO_3^-
$NaBrO_3$	6 N NaOH	2.5	25°	100% BrO_3^-
$NaBrO_3$	6 N NaOH	8	25°	100% BrO_3^-
$KBrO_3$	conc. KOH	3	orange KO_3 formed in delivery tube, 25°	100% BrO_3^-
$NaIO_3$	1 N NaOH	4	15 gm. at 80°	31% yield $Na_2H_3IO_6$
$NaIO_3$[a]	6 N NaOH	3	5 gm. at 25°	20% yield $Na_2H_3IO_6$
$NaIO_3$[a] $NaBrO_3$ }	6 N NaOH	4.5	{ 10.00 gm. $NaIO_3$ 5.00 gm. $NaBrO_3$ }	18% $Na_2H_3IO_6$, no BrO_4^-
$NaIO_3$[a] $NaBrO_3$ }	1 N NaOH	8	{ 0.5 gm. $NaIO_3$ 5.0 gm. $NaBrO_3$ }	100% $Na_2H_3IO_6$
$NaIO_3$[a]	0.1 N HNO_3	3	25°	trace IO_4^-
$NaClO_3$	0.1 N HNO_3	3	25°	some ClO_4^-
$KClO_3$	conc. H_2SO_4	0.5	dry ice-acetone bath	decomposed
$KBrO_3$	conc. H_2SO_4	0.5	dry ice-acetone bath	decomposed
KIO_3	conc. H_2SO_4	0.5	dry ice-acetone bath	no change
$NaIO_3$	conc. H_2SO_4	0.5	hot turned yellow	no change
Br_2	conc. H_2SO_4	0.5	dry ice-acetone bath	no change
$NaIO_3$	40% H_2F_2	1	dry ice-acetone bath	no change
$KBrO_3$	40% H_2F_2	1	dry ice-acetone bath	slowly decomposed
$KBrO_4$	72% $HClO_4$	0.5	dry ice-acetone bath	decomposed
$KBrO_3$	conc. $HC_2H_3O_2$	2	0°	no change
$AgIO_3$	conc. NH_4OH	1	25°	no change
$AgBrO_3$[a]	conc. NH_4OH	1	25°	no change

[a]Residues were further checked under the microscope and with spot tests.

would probably be more stable at lower temperatures. Attempts were made to oxidize bromates with ozone in glacial acetic, 48% hydrofluoric, concentrated sulfuric, and 72% perchloric acids at the temperature of dry ice and acetone. Hydrofluoric and acetic acids, being weak, did not decompose the bromate readily. The strong acids decomposed the bromates and chlorates even at the very low temperatures. Sidgewick[39] states that in concentrated hydrofluoric acid solutions, bromic acid forms this ion, $(H_2BrO_3)^+$. If oxidation would take place, $(H_2BrO_4)^+$ might form in the acid solutions and be stable at the low temperatures.

Oxidation experiments in aqueous solvents, as well as in liquid ammonia, gave much poorer results than expected; and no evidence was found for the formation of perbromates in the experiments listed in Table 7.

5. Catalysts used

The silver ion is a well known catalyst for the formation of permanganates in acid solutions when persulfates are used as the oxidizing agent. The silver ion catalyst has been used in the ozone oxidation of chlorates to perchlorates by Bennett and Mack,[35] who report yields of 2% with the catalyst. The silver ion is said to be oxidized in acid solutions to Ag^{++} or AgO^+, and these in turn oxidize the chlorates to perchlorates. It would seem that if the oxidation potential of the oxidant were high enough to form a new oxidant (Ag^{++} or AgO^+), it should also be able to oxidize the chlorate directly to the perchlorate. Noyes[55] has shown that in acid solutions of silver nitrate a large amount of Ag^{++} is present. In neutral solutions AgO is precipitated as a black powder,

according to Noyes.[55]

The cobaltic ion, though relatively unstable in aqueous solutions, can be formed in aqueous solutions by electrolysis.[56] Its high potential would also make it a possible oxidation catalyst. $Co(ClO_3)_2 \cdot 6H_2O$ and $Co(BrO_3)_2 \cdot 6H_2O$ were both prepared as described under section II, A. "Materials Used"; but they were both quite easily decomposed and unstable in the dry state.

Latimer[9] gives the following values for the silver and cobalt oxidation potentials:

$$Co^{+++} + e \longrightarrow Co^{++} \qquad E^0 = 1.84 \text{ volts}$$

$$Co(OH)_3 + e \longrightarrow Co(OH)_2 + OH^- \qquad E^0 = 0.2 \text{ volts}$$

$$Ag^{++} + e \longrightarrow Ag^+ \qquad E^0 = 0.193 \text{ volts}$$

$$AgO^+ + e + 2H^+ \longrightarrow Ag^{++} + H_2O \qquad E^0 = 2.1 \text{ volts (calc.)}$$

$$AgO^+ + 2H^+ + 2e \longrightarrow Ag^+ + H_2O \qquad E^0 = 2.0 \text{ volts (calc.)}$$
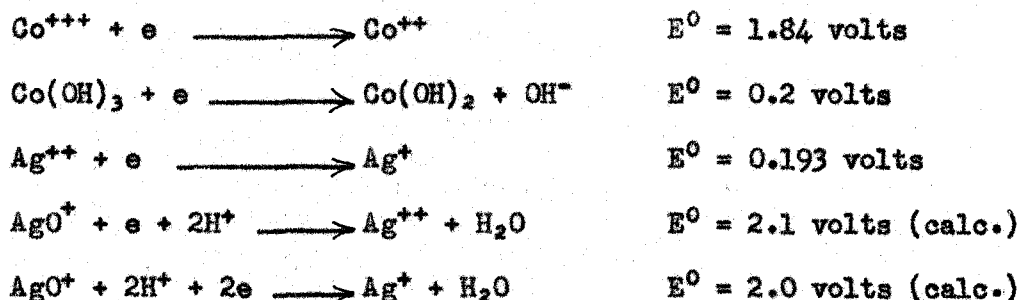
Table 8 indicates typical examples of the experiments performed using ozone in the presence of catalysts. Much time was necessary for the formation of much brown color or black AgO in the solutions, which indicated a slow formation of argentic ions by the ozone.

Several things might be mentioned in connection with the individual experiments: first, silver bromate was moderately soluble in nitric acid solutions; and, as long as any brown color was present in the solutions, no decomposition took place. The bromine was all present, apparently as bromate. Before and after the brown color was formed in the solutions, however, bromic acid decomposed.

Second, in the neutral and alkaline solutions, tests were made for

Table 8

Substance	Time (hrs.)	Solvent	Catalyst	Analysis
$KBrO_3$[a]	2	conc. HNO_3	0.1 gm. $AgNO_3$	decomposed
$KClO_3$[a]	$2\frac{1}{2}$	conc. HNO_3	0.1 gm. $AgNO_3$	trace ClO_4^-
KIO_3[a]	$2\frac{1}{2}$	conc. HNO_3	0.1 gm. $AgNO_3$	no IO_4^-
$AgBrO_3$	4	H_2O	- - -	100% BrO_3^-
$AgIO_3$	3	H_2O	- - -	9.1% IO_4^-
$NaClO_3$	5	H_2O	1.0 gm. $AgNO_3$	trace ClO_4^-
$KBrO_3$[a]	$3\frac{1}{2}$	1 N KOH	0.1 gm. $AgNO_3$	100% BrO_3^-
$KClO_3$[a]	3	1 N KOH	0.1 gm. $AgNO_3$	no ClO_4^-
KIO_3[a]	$3\frac{1}{2}$	1 N KOH	0.1 gm. $AgNO_3$	14% IO_4^-
$NaBrO_3$	6	H_2O	UV-rays	no change
$KClO_3$	$4\frac{1}{2}$	H_2O	UV-rays	no change
$Co(BrO_3)_2 \cdot 6H_2O$	3	H_2O	- - -	no change
$Co(ClO_3)_2 \cdot 6H_2O$	3	H_2O	- - -	no change
$NaBrO_3$	2	0.01 N NaOH	trace Co^{++}	no change
$NaClO_3$	2	0.01 N NaOH	trace Co^{++}	no change

[a]Similar experiments were made using sodium salts.

the various ions on solutions, white residues, and hot water extracts
from the residues. This was done so that the black AgO precipitate would
not have to be destroyed before analysis for the perbromate ion was attemp-
ted. Analysis for the halate ions was usually carried out by liberating
iodine from potassium iodide and titrating with thiosulfate. Residues and
precipitates where possible were separated, given spot tests, and a micro-
scopic examination.

Third, the cobalt salts used gave no evidence of being active under
the conditions used.

Fourth, ultraviolet light was used since it is reported to activate
ozone by aiding in a more rapid rate of decomposition of ozone into atomic
oxygen. Sodium bromate was irradiated for six hours while ozone was
being passed into the solution. The solution, after the removal of the
excess ozone by the passage of oxygen through the solution for 15 minutes,
was analyzed for total oxidizing power. Further examination was made of
the crystals obtained by evaporation of the water. Sodium bromate forms
isotropic crystals; therefore this residue was examined with polarized
light and found to contain some anisotropic material. However, it was
very finely divided and of such small amount that it may well have been
impurities from dust, dissolved silica, etc. None of the organic reagents
or spot tests gave any evidence to support the conclusion that perbromate
was present in the residue.

Fifth, in some experiments using the silver ion in fairly large
amounts, extractions of the residues and solutions with toluene and ether
were used. Silver perchlorate is quite soluble in these solvents - espe-
cially toluene. Silver perchlorate was found to be extracted when its

concentration was large enough, but no perhalate was found to be present in these experiments by this method.

6. Discussion of results

Ozone oxidation of iodates to periodates gave good yields in alkaline solutions; but other halates were oxidized only in very small amounts, if at all, even with catalysts. A number of other catalysts were tried - hopcalite, vanadium pentoxide, silver vanadate, and platinum vessels - but none of them gave any indication of aiding the oxidation of the halates or halides to perhalates.

D. Peroxydisulfate Oxidation

1. General considerations

Peroxydisulfate, with an oxidation potential of 2.05 volts for the reaction $S_2O_8^= + 2e \longrightarrow 2SO_4^=$, is just about equal to ozone as an oxidizing agent. The ammonium and potassium salts, being solids and fairly stable to heat, offered the possibility of oxidation in the fused state as well as in solution. Large yields of argentic ions in solutions and precipitates are very easy to obtain with peroxydisulfates. The usual method for the removal of excess peroxydisulfate is by boiling; however, if perbromates are unstable to heat, this would also decompose the perbromates if formed. Peroxydisulfates and bromates in neutral solutions react slowly to liberate bromine, especially if the solutions are concentrated or warmed.

2. Catalysts used

The silver ion was the catalyst used in the experiments, and the data are tabulated in Table 9. The procedures, in general, were to use the halides or halates in acid or basic solutions with small or large amounts of silver nitrate, and boil the solutions with solid ammonium or potassium peroxydisulfate. In nitric acid solutions, the color of the argentic ions is quite dark, but in basic solutions the solutions are colorless as long as only a small amount of silver ion is present. Large amounts of silver nitrate in basic or neutral solutions gave precipitates of black AgO.

The bromates were stable in alkaline solutions, and were stable in acid solutions only as long as the oxidizing conditions remained. When solutions of potassium bromide, potassium bromate, or silver bromate were boiled in the presence of large amounts of silver ions and peroxydisulfates, a white precipitate in a brown colored solution would be seen. As soon as the peroxydisulfate was decomposed and the brown color of argentic ions disappeared, a yellow precipitate of silver bromide would appear as the bromate decomposed to bromide and bromine. The brown color was slow to fade in cold solutions, but 30% hydrogen peroxide caused it to immediately fade and a yellow silver bromide was formed as the bromate was reduced. This action of 30% hydrogen peroxide was used as a qualitative test for the presence of silver bromate or silver periodate in nitric acid solutions, especially when peroxydisulfate or argentic ions were still present.

Bennett and Mack[35] reported an 18% yield of perchlorate when peroxydisulfate was used alone, but the addition of the silver ion as a catalyst

Table 9

Experiments with Peroxydisulfate Oxidation

Substance	Solvent	Catalyst	Remarks	Analysis
$NaIO_3$	dil. NaOH	none	large ppt. $Na_3H_2IO_6$	- - -
$NaBrO_3$	dil. NaOH	none	no ppt.	100% BrO_3^-
$KClO_3$	dil. KOH	none	white ppt. $KClO_4$	5% ClO_4^-
$KClO_3$	dil. KOH	Ag^+ trace	white ppt. $KClO_4$	20% ClO_4^-
$NaIO_3$ $NaBrO_3$}	dil. NaOH	Ag^+ trace	large ppt. $Na_3H_2IO_6$	IO_4^- and BrO_3^-
$NaClO_3$ $NaBrO_3$}	dil. NaOH	Ag^+ trace	small ppt. $KClO_4$	no BrO_4^-
KI	3 N HNO_3	1 gm. $AgNO_3$	brown solution	IO_3^-
KCl	3 N HNO_3	1 gm. $AgNO_3$	brown solution	trace ClO_4^-
KBr	3 N HNO_3	1 gm. $AgNO_3$	brown solution	BrO_3^-
KIO_3	3 N HNO_3	1 gm. $AgNO_3$	brown solution	some IO_4^-
$KClO_3$	3 N HNO_3	1 gm. $AgNO_3$	brown solution	trace ClO_4^-
$KBrO_3$	3 N HNO_3	1 gm. $AgNO_3$	brown solution	BrO_3^-
$AgIO_3$	3 N HNO_3	none	brown solution	no change
$AgBrO_3$	3 N HNO_3	none	brown solution	no change
KI	1 N KOH	Ag^+ trace	- - -	KIO_3 and $KClO_4$
KBr	1 N KOH	Ag^+ trace	- - -	$KBrO_3$
KCl	1 N KOH	Ag^+ trace	- - -	$KClO_3$ and $KClO_4$

increases the yield to 30%. The writer found the same general relationships to be true. Periodates were found to be formed very readily in alkaline solutions, both with and without a catalyst. Potassium peroxydisulfate and silver nitrate in dilute potassium hydroxide were heated; and, after black AgO formed, hot potassium iodide was added and heating continued until the peroxydisulfate was decomposed. The silver ion was precipitated by adding sodium chloride, and an analysis of the solution showed the presence of iodates and periodates. Analyses of several runs showed the presence of from 25% to 50% yields of periodate. When potassium bromide was used, the analysis gave the theoretical amount of potassium bromate as calculated from the known weight of the potassium bromide used. Using 0.644 grams of potassium bromide, the thiosulfate titration showed 0.638 grams of potassium bromate formed. Precipitates of potassium perchlorate and tertiary sodium paraperiodate were prepared by oxidation with peroxydisulfate in the presence of some bromate. The resulting precipitates were analyzed for any bromine content, in case perbromates were coprecipitated with the perchlorate or periodate.

The perchlorate precipitate was analyzed by reducing any bromine salt with hydrogen peroxide in nitric acid and precipitating the bromide with silver nitrate. The solution was then evaporated to dryness, fused with sodium carbonate, and the solution of this residue was treated with carbon tetrachloride and chlorine water. Another sample was analyzed for total oxidizing power by titrating the liberated iodine with thiosulfate.

The periodate precipitate was analyzed for total oxidizing power by treating with potassium iodide in an acid solution and titrating the liberated iodine with thiosulfate. The periodate content was determined by

titrating with arsenite solution in a solution buffered with sodium bi-
carbonate. No bromine was found in either of the precipitates. A few
residues and precipitates were given microscopic examination and treated
with organic spot test reagents. This was of little value, since most of
the reagents which react with the perhalates also react similarly with
peroxydisulfate, which was often present.

3. Experiments in non-aqueous solvents

Since peroxydisulfates readily decompose bromates with the liberation
of bromine in acid solutions and even in warm neutral solutions, it was
hoped to allow the peroxydisulfate to react with the bromate in non-
aqueous solvents. Table 10 shows some of the solvents used and the
results.

The peroxydisulfate decomposed the bromate in all experiments and
liberated bromine, which then reacted with some of the solvents. In the
case of bromate in acetone, a pink color and pink precipitate was formed;
and the solution gave off vapors which had pronounced lachrymal proper-
ties. This latter is characteristic of substitution products of bromine
and acetone. The pink solid mixture of peroxydisulfate and bromate was
very unstable, and drying on a warm hot-plate was enough to cause a vio-
lent decomposition reaction liberating bromine and oxygen. When potassium
instead of ammonium peroxydisulfate was used with potassium bromate, no
pink solution or pink residue was formed. This seemed to indicate that
the ammonium ion has an active part in forming the pink color. Another
unusual aspect was the dominance of a yellow color in the acetone when

Table 10

Experiments with Peroxydisulfate Oxidation in Non-aqueous Solvents[a]

Sub-stance	Solvent	Remarks
$NaBrO_3$	water	decomposes slowly to give Br_2
$NaBrO_3$	95% ethanol	yellow solution
$NaBrO_3$	absolute ethanol	yellow solution
$NaBrO_3$	methanol	yellow solution
$NaBrO_3$	acetone	pink solution and residue
$NaBrO_3$	ethyl acetate	yellow solution
$NaBrO_3$	CCl_4	orange-colored solution
$NaBrO_3$	toluene	colorless to yellow solution
$NaBrO_3$	dioxane	colorless
$NaBrO_3$	ether	colorless
$NaBrO_3$	ammonia	no apparent reaction
$KBrO_3$	acetone	pink solution and residue
$KBrO_3$[b]	acetone	yellow color only
$KBrO_3$	acetone, excess $(NH_4)_2S_2O_8$	pink color in solvent
$KBrO_3$	acetone, excess $KBrO_3$	yellow color in solvent

[a]Time of standing was from 36 to 48 hours in each experiment.

[b]$K_2S_2O_8$ was used.

potassium or sodium bromate was present in excess and a pink color when ammonium peroxydisulfate was present in excess.

It was difficult to use many of the proposed methods of analysis due to the presence of the peroxydisulfate ion. Many of the organic reagents gave similar tests with the perhalate ions as with the peroxydisulfate ion. Extraction with various solvents gave negative results. Some of the qualitative tests could be used, and a microscopic examination was made on the residues. No evidence was found that would indicate the presence of any ions other than the ones known to be present in the mixtures.

4. Related experiments

When ammonium and potassium peroxydisulfates were heated with the halates in the dry state, the halogen was readily set free.

AgO was prepared with peroxydisulfates in neutral solutions of silver nitrate as suggested by Noyes.[56] The black AgO precipitate was dried and heated with the halates.

Sodium bismuthate was heated with the halates in the dry state; it was also used in concentrated nitric acid solutions with the silver ion to oxidize the halides. Potassium iodide, sodium chloride, and sodium bromide were all oxidized to the halates by this procedure. The periodate was formed in neutral solutions, but the perchlorate and perbromate were not found to be formed. The bismuthate readily oxidized the silver ion to the higher valences. Table 11 shows the data for experiments conducted with sodium bismuthate. These solutions were permitted to stand one week,

Table 11

Experiments with Sodium Bismuthate Oxidation[a]

Substance	Solvent	Qualitative Analysis
KI	Conc. HNO_3	IO_3^-
NaCl	Conc. HNO_3	ClO_3^-
NaBr	Conc. HNO_3	BrO_3^-
KI	72% $HClO_4$	IO_3^-
KBr	72% $HClO_4$	BrO_3^-
$KBrO_3$	72% $HClO_4$	only BrO_3^-
KI	H_2O	IO_3^- and IO_4^-
KBr	H_2O	BrO_3^-
$KBrO_3$	H_2O	only BrO_3^-
KCl	H_2O	some ClO_3^-
$KClO_3$	H_2O	no ClO_4^-

[a]Relatively large amounts of sodium bismuthate
were added in each experiment along with 0.1
gram of silver nitrate as a catalyst. Solutions
were all heated some during the seven day
period.

and only qualitative tests were made on the solutions. The black precip-
itates and dark colored argentic ions were present in the solutions during
the entire time. The results indicate that bismuthates are capable of
easily oxidizing the halides to halates, and silver to its higher valen-
ces; but no evidence of perbromates or perchlorates could be found.

When solid sodium bismuthate was fused with silver bromate, bromine
was liberated as the bromate was decomposed. This is similar to the
action of persulfates on the halates when heated together.

5. Discussion of results

Peroxydisulfates proved themselves very capable of oxidizing iodine
to the plus five and plus seven oxidation states, and to a lesser extent
oxidized chlorine to the plus seven oxidation state. The silver ion
catalyst proved an aid in obtaining higher yields with peroxydisulfates.
The difficulty in analyzing the mixtures, and the liberation of the free
halogen from mixtures of halate and peroxydisulfate, were the main dis-
advantages encountered.

E. Fluorine Oxidation

1. General considerations

The high oxidation potentials of elemental fluorine gas (see Table 1),
the oxidizing power of water solutions of fluorine, and the accompanying
presence of fluorine oxide in alkaline solutions, all gave considerable
hope of success for the preparation of perhalates by fluorine oxidation.

Early study of the use of fluorine as an oxidizing agent was carried out by Fichter and Brunner[57] in which they oxidized manganous ions to permanganates, chromic ions to dichromates, sulfate ions to peroxydisulfates, cobaltous sulfate to cobaltic sulfate, carbonates to percarbonates, and borates to perborates in aqueous solutions. Another worker was Jones[58] who concluded that fluorine oxidation in aqueous solution produced the same results as anodic oxidation plus disturbances due to the presence of hydrofluoric acid which is formed, and that many oxidations can be brought about by bubbling fluorine through acidic or basic solutions.

A recent complete presentation of the preparation, handling, and use of fluorine was given at the 110th meeting of the American Chemical Society.[7] The use and handling of fluorine gas does require special techniques,[59] due to its extreme chemical reactivity as well as its toxicity. Small amounts of fluorine gas are detected by its reaction with potassium iodide paper or its reaction with ammonia fumes. The gas can be disposed of by passing it into sodium hydroxide solutions, or by passing it into sodium chloride and the liberated chlorine trapped in soda lime.

Anhydrous fluorinating and oxidizing agents are prepared using fluorine gas; i. e., $F_2 + CoF_2 \longrightarrow CoF_3$, $AgF + F_2 \longrightarrow AgF_2$, and $MnF_2 + F_2 \longrightarrow MnF_3$. Sidgwick[25] gives other reactions involving fluorine and the other halogens in which chlorine trifluoride, bromine pentafluoride, and iodine heptafluoride are formed. These react vigorously with water, except for iodine heptafluoride which reacts only slowly. There

is a tendency for the higher valence to be possible with iodine, but plus

five is the highest valence with bromine and plus three is the highest

valence possible with chlorine. In the anhydrous state, fluorine reacts

with iodine to give a maximum oxidation state of seven (IF_7); with

Table 12

Bond Lengths for Some Atoms

Element	Radius($\overset{o}{A}$)	Compound and bond length ($\overset{o}{A}$)					
F	0.64	-	-	IO_6^{-5}	1.93	-	-
O	0.66	OF_2	1.42	-	-	-	-
Cl	0.99	ClF_3	-	ClO_4^-	1.48	ClO_3^-	1.48
S	1.04	SF_6	-	SO_4^{--}	1.51	SO_3^{--}	1.4
P	1.10	PF_5	1.52	PO_4^{---}	1.55	-	-
Br	1.11	BrF_5	-	BrO_4^-	-	BrO_3^-	1.68
I	1.28	IF_7	-	IO_4^-	1.79	IO_3^-	1.8

bromine, fluorine gives a maximum oxidation state of five (BrF_5); and

with chlorine only ClF_3 has been formed. The existence of BrF_5 indicates

the possibility of bromine being capable of holding four oxygen atoms co-

valently around it. The comparison of some covalent radii[60] and some

known compounds support the assumption that, from the standpoint of size

considerations, bromine should hold four oxygens easily. (See Table 12.)

Fluorine reacts with aqueous solutions to give several products,

depending on the acidity or alkalinity of the solution. Oxygen fluoride is always a product but is produced up to 70% in 2% sodium hydroxide solutions; whereas in neutral solutions it is produced in yields of 1% or less. The oxygen fluoride produced further reacts to liberate oxygen and to form hydrofluoric acid. Early work with fluorine indicated ozone and hydrogen peroxide were produced in aqueous solutions; however, conflicting results have been recently reported. Cady[61] states that if ozone is produced at all, it is in very small amounts. Hückel[62] suggests that ozone may be produced when fluorine reacts with ice at temperatures between $0°$ and $-50°$, but is not produced above $0°$ in aqueous solutions. All the above workers agree on the formation of some hydrogen peroxide in the reactions, and Fichter and Arnal[63] report that it is impractical to prepare periodic acid with fluorine because of the ability of the hydrogen peroxide formed to reduce periodic acid. However, a 48% yield of potassium periodate was obtained by them in a 2 N potassium hydroxide solution using fluorine gas. Concentrated nitric and perchloric acids are not suitable solvents to use with fluorine, since explosive $F \cdot NO_3$[64] and $F \cdot ClO_4$[65] gases are formed.

The catalysts commonly used in fluorination[59] and the ones having the highest oxidation potentials (see Table 1) are the silver ion and cobalt ion. These were used in the form of silver nitrate, silver bromate, silver iodate, cobalt bromate, cobalt chlorate, and cobalt nitrate.

2. Chlorine oxidation

Chlorine gas was used in a number of experiments (Table 13) in order

Table 13

Experiments with Chlorine Oxidation[a]

Substance	Solvent	Results
I_2	NaOH	much $Na_3H_2IO_6$ ppt. formed
KI	NaOH	much $Na_3H_2IO_6$ ppt. formed
$NaIO_3$ $NaBrO_3$	NaOH	much $Na_3H_2IO_6$ ppt. formed
Br_2	NaOH	some $NaBrO_3$ formed
Br_2	KOH	some $KBrO_3$ formed
Br_2 $KClO_4$	KOH	$KClO_4$ and $KBrO_3$ ppt. formed
Br_2	$Ba(OH)_2$	$Ba(BrO_3)_2$ ppt. formed
Br_2	BaO_2	$Ba(BrO_3)_2$ ppt. formed
KBr	NaOH	$KBrO_3$ ppt. formed
KBr	$NaHCO_3$	$KBrO_3$ ppt. formed
$KBrO_3$	KOH	no change
$KBrO_3$	72% $HClO_4$	decomposed
$KBrO_3$	48% H_2F_2	decomposed

[a]Stoichiometric amounts of reactants were used and then chlorine was passed through the solution until a neutral solution was obtained.

to become familiar with procedures which would be used with fluorine. Chlorine has long been used for preparing periodates, as described by Hill;[66] and, of course, chlorine probably should be capable of oxidizing bromates to perbromates.

Chlorine was bubbled into solutions containing iodine and bromine in their several oxidation states and usually in a basic solution. In general, hot solutions were used for the reactions; and when the alkaline solutions became neutral the reactions were stopped.

Examination and an analysis was carried out on the solid precipitate formed by evaporation and cooling. Then a precipitate was obtained by adding an alcohol-acetone mixture to each filtrate and this precipitate was examined and analyzed.

Periodates, as well as bromates, were readily formed by chlorine oxidation; but no evidence of perbromates was found.

Weighed portions of each residue were analyzed for total oxidizing power by titrating liberated iodine with thiosulfate. Periodates were treated with potassium iodide in a sodium bicarbonate buffered solution, and the liberated iodine titrated with arsenite solution.

Qualitative spot tests were made on the residues, precipitates, and solutions. Silver nitrate produced colored precipitates with the bromide, iodide, and periodate ions; and white precipitates with the chloride, bromate, and iodate ions. The manganous sulfate-phosphoric acid reagent gives a characteristic red color with bromate and periodate ions in the cold, and a red color with the chlorate ion when heated. Various tests were made with organic reagents as discussed under section II, B.

3. **Apparatus used**

A steel tank containing one-half pound of fluorine was obtained from Pennsylvania Salt Manufacturing Company. A brass needle valve was re-packed with lead packing and fitted on a Monel Metal adaptor leading from the tank. All connections required lead washers with copper or brass pipe. For most of the experiments a copper tube joined to a glass tube by a joint of plaster of paris was used to conduct the gas into the reaction vessel. The fluorine gradually weakened the plaster of paris where it came in contact with it, and numerous replacements were necessary. Later, tetrafluorethylene ("Teflon," E. I. duPont de Nemours and Co.) tubing was available and was threaded to fit the brass outlet tube to conduct the fluorine into the solutions. Even this material was attacked by the fluorine gas after long usage. For some experiments the glass vessels and delivery tubes were coated with paraffin to resist the action of the fluorine solutions on the glass; but, for the most part, this was not con-sidered to be a necessary precaution against contamination.

4. **Experiments without catalysts**

It will be seen from the data in Table 14 that, as was expected, oxidation with fluorine gas proceeded at a much faster rate than with chlorine or ozone in aqueous solutions. Manganese, cobalt, chromium, silver, sulfur, and selenium compounds were used to confirm the statement that fluorine oxidizes elements to their highest oxidation state. Sele-nium has not as yet been oxidized to the perselenate state as sulfur has. Alkaline solutions were best for preparing the periodates, whereas acidic

Table 14

Experiments with Fluorine Oxidation[a]

Substance	Solvent	Time (hrs.)	Remarks
$NaIO_3$	dil. HNO_3	3/4	no periodate formed
$NaIO_3$	6 N NaOH	3/4	70% yield periodate
$NaClO_3$	10% $NaHCO_3$	3/4	no perchlorate formed
$KClO_3$	dil. HNO_3	1	10% yield perchlorate
$CoSO_4$	H_2O	-	dark color Co^{+++} formed
$MnSO_4$	dil. H_2SO_4	-	permanganate formed
$KHSO_4$	H_2O	-	peroxydisulfate formed
K_2SeO_3	dil. KOH	-	selenates (no perselenates)
$Cr_2(SO_4)_3$	dil. H_2SO_4	-	dichromate formed
$AgNO_3$	H_2O	-	Ag_2O_2 formed
$KClO_3$	2% KOH	1/2	no change
KCl	50% KOH	1/2	some chlorates formed
KIO_3	2% KOH	1/2	16% yield periodate
KI	50% KOH	1/2	96% yield iodate
$NaIO_3$	10% $NaHCO_3$	1/2	62% yield periodate
$NaClO_3$	H_2O	1/2	trace perchlorate

[a]Numerous explosions giving off light were produced while bubbling the fluorine through the solutions.

solutions were best for forming perchlorates; however, poor yields of the latter were obtained. One reason for the poor yields was the length of time for the treatment. This was kept short due to the reaction of the hydrofluoric acid produced in the reaction of fluorine with water; the necessity of keeping the solution from becoming acidic, in the case of bromine; and the fact that at varying intervals small explosions, giving off light, occurred in the solutions. These explosions sometimes caused a loss of solution. The explosions occurred in all the solutions irregardless of the substances present, and the nature of these explosions is unknown. It has been reported[67] that fluorine in moist air gives sparks and flashes, and also that the reaction between fluorine and water is erratic and not a smooth reaction.

Organic solvents were not used because of the danger of explosions; and even carbon tetrachloride, which was thought to be safe, reacted very violently.

When fluorine reacts with strongly alkaline solutions, there is produced an oxidizing substance which is very difficult to remove. Dennis and Rochow[68] treated a 50% potassium hydroxide solution with fluorine, evaporated the solution to dryness, and fused the residue in an open flame. The fused material still had oxidizing power. They concluded that under these conditions the oxidizing power could not be hydrogen peroxide, ozone, or oxygen fluoride. Oxygen fluoride is decomposed readily by concentrated hydroxide solutions.

In a further experiment, Dennis and Rochow[68] electrolyzed a molten mixture of potassium fluoride and potassium hydroxide in a silver

crucible. They obtained a substance which formed a precipitate with the silver ion and gave indications of being $AgFO_3$. Microscopic examination showed two kinds of crystals, isotropic silver chloride crystals and anisotropic $AgFO_3$ (?) crystals. Refractive indices of silver bromate, silver chlorate, and $AgFO_3$ (?) were compared and found to be as expected. They feel the results of their experiments are strongly indicative of the formation of an oxysalt of fluorine.

Another source of difficulty in the present work was the necessity of destroying hydrogen peroxide which formed in neutral or acidic solutions. Bubbling oxygen through the solutions for several hours removed the gases; boiling the solutions decomposed the hydrogen peroxide formed; but the unknown oxidizing agent, remaining in at least the strongly basic solutions, was not removed by this treatment. Whatever the oxidizing substance is, it made the method of analysis of total oxidizing power much less applicable to the detection of perbromates in these experiments.

Since fluorine rather easily oxidized the iodates and chlorates to the perhalates, a series of experiments were attempted on bromates. Table 15 gives data on kinds of solutions used and other details. Basic solutions were used due to the decomposition of bromates in acid solutions. Over the long periods of the addition of fluorine, some base had to be added to keep the solution from becoming acidic; and this produced large amounts of the metal fluoride. Some sodium fluosilicate was also formed due to the reaction with the glass containers. Paraffin coated flasks were used occasionally at the lower temperatures.

Evaporation of the solution caused potassium bromate to be precipi-

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Table 15

Experiments with Fluorine Oxidation without Catalysts

Sub-stance	Solvent	Time (hrs.)	Temperature	Results
$KBrO_3$	2% KOH	1	25^0	no change
$KBrO_3$	2% KOH	1	$90^0 - 100^0$	no change
$KBrO_3$	50% KOH	1	$90^0 - 100^0$	no change
$KBrO_3$	50% KOH	1	0^0	no change
$NaBrO_3$	satd. NaOH	3	dry ice-acetone bath	no change
$NaBrO_3$	H_2F_2 48%	3	dry ice-acetone bath	decomposed
Br_2	H_2F_2 48%	3	dry ice-acetone bath	no bromate
$NaBrO_3$	satd. $NaHCO_3$	$1\frac{1}{2}$	25^0	no change
$NaBrO_3$	satd. $NaHCO_3$	2	$90^0 - 100^0$	no change
$KBrO_3$	K_2CO_3	3	90^0	no change
$KBrO_3$	6 N KOH	4	25^0	no change
$NaBrO_3$[a]	H_2O	$\frac{1}{4}$	25^0	no change
$NaBrO_3$[a]	1 N NaOH	$\frac{1}{2}$	25^0	no change
$NaBrO_3$[b]	1 N NaOH	$\frac{1}{2}$	25^0	no change

[a]Teflon delivery tube and teflon reaction vessel was used so that upon evaporation only isotropic crystals could be present, namely, $NaBrO_3$ and NaF. Microscopic examination confirmed the presence of only isotropic crystals.

[b]Teflon delivery tube and Pt reaction vessel gave the same results.

tated from the potassium hydroxide solutions leaving the potassium fluoride in solution. Large quantities of sodium fluoride and some sodium fluosilicate were precipitated from solutions containing the sodium ion. The dissolved salts could then be precipitated from the remaining solution by adding alcohol and acetone.

The residues and precipitates were examined under the microscope with organic reagents and spot tests. The total oxidizing power toward acid and alkaline potassium iodide was determined. No evidence of any decomposition of bromate was found except when the solution was allowed to become neutral or acidic. No evidence was found for the formation of perbromates.

5. Experiments with catalysts

Data from experiments with silver and cobalt as catalysts are compiled in Table 16. These catalysts seemed to increase the rate of perchlorate formation slightly with fluorine oxidation. No attempt was made to obtain high yields of perchlorates, but a 94% yield of periodate was obtained using silver nitrate and passing fluorine through an alkaline solution for two hours.

The silver was removed from the acid solutions by precipitating with excess sodium chloride; then aliquot portions of the filtrate were:
(a) titrated with 0.1 N silver nitrate to determine the chloride; (b) reduced with sulfur dioxide, boiled, and the chloride determined; and
(c) evaporated to dryness, fused with sodium carbonate, and the chloride determined on a solution of the residue. The chlorate and perchlorate

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Table 16

Experiments with Fluorine Oxidation with Catalysts

Substance	Wt. (gm.)	Solvent	Time (hrs.)	Remarks	Analysis
$NaClO_3$[a]	5	dil. HNO_3	1/3	brown color	4.8% ClO_4^-
$KClO_3$[a]	5	dil. H_2F_2	1	brown color	8.1% ClO_4^-
$NaClO_3$[b]	2	dil. HNO_3	1/2	deep red color	8.4% ClO_3^-
$KClO_3$[b]	2	dil. H_2F_2	1/2	deep red color	6.6% ClO_4^-
$Co(ClO_3)_2$	10	dil. HNO_3	3/4	deep red color	10.9% ClO_4^-
$AgClO_3$	5	dil. HNO_3	3/4	brown color	9.3% ClO_4^-
$NaBrO_3$[a]	5	NaOH	3	- - -	no BrO_4^-
$NaBrO_3$[a]	5	NaOH	2	black ppt.	no BrO_4^-
$KBrO_3$	5	KOH	2	black ppt.	no BrO_4^-
$AgBrO_3$	3	NaOH	1	black ppt.	no BrO_4^-
KIO_3[a]	5	KOH	2	black ppt.	94% IO_4^-
$AgBrO_3$	3	dil. HNO_3	1	brown color	decomposed
$AgBrO_3$	3	dil. H_2F_2	1	brown color	decomposed
$KBrO_3$[a]	5	dil. HNO_3	1	brown color	decomposed
Br_2[a]	2	dil. HNO_3	1/4	neutralized KOH	some BrO_3^-
$KBrO_3$[b]	2	dil. H_2F_2	1/2	deep red color	no BrO_4^-
$Co(BrO_3)_2$	8	dil. NaOH	1/2	brown color	no BrO_4^-
$KClO_4$[b]	10	H_2O (70°)	1/4	deep red color	no BrO_4^-

[a]One gram of silver nitrate was used as catalyst.

[b]Four grams of cobalt halate were used as catalyst.

were calculated by the difference in the chloride titrations. A Mohr's end point of silver chromate was used for most determinations.

The bromate solutions which were basic usually contained precipitates of black AgO and white silver bromate. Hot water was used to leach out the silver bromate, and the bromate was subsequently determined by liberating iodine from potassium iodide and titrating with sodium thiosulfate. Most of the analyses gave the theoretical amount of bromate that was expected within experimental error; some few differences were traced to loss.

The acid solutions containing cobalt as a catalyst showed a deep red color forming as soon as fluorine was admitted to the solution, and the color soon disappeared after fluorine was stopped. This is evidently due to the formation of the cobaltic ion in some form in the solution. The large amounts of cobalt ion were precipitated from the solutions by adding sodium bicarbonate, and filtering off the hydroxide and sodium fluoride. The chlorate, perchlorate, and chloride concentrations were determined as above with silver nitrate titration after reduction of the ions to the chloride.

Residues or precipitates from the solutions were examined with organic reagents under the microscope. The methylene blue test, which forms a pink precipitate for perchlorate and persulfate ions, gave a pink precipitate with several of the residues. This was a possible indication of perbromate. Further investigation, however, showed that solutions involving similar mixtures with bromine absent gave the same methylene blue test. Probably fluorine was responsible for the color.

Each mixture was examined and tested under the microscope with the organic reagents listed in section II, B. The results were compared with a similar examination of the ions which were known to be present in each mixture. No evidence of the presence of perbromates could be detected.
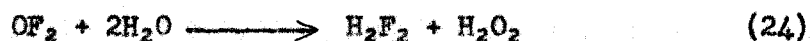
6. Discussion of results

There seems to be no question as to the ability of fluorine to oxidize elements to their higher oxidation states. As in previous experiments, the basic solution was seemingly essential because of the instability of bromic acid.

The several difficulties in the use and handling of fluorine coupled with its rather violent reaction occasionally in water solutions, made necessary the running of a large number of experiments in which precise information was difficult to obtain. Nevertheless, the conclusion seems valid that the oxidation potential for perbromates is extraordinarily high, or that perbromates are unstable in aqueous solutions.

Fluorine gas is not applicable for use in liquid ammonia or in most organic solvents because of its reactivity.

As has been mentioned, fluorine reacts with moist air and water in an erratic manner; and in the experiments carried out in this work, explosions which gave off light were common. The following equations were written in an attempt to suggest a possible cause for the explosions.

$$2F_2 + H_2O \longrightarrow H_2F_2 + OF_2 \tag{16}$$

$$F_2 + 2H_2O \longrightarrow H_2F_2 + H_2O_2 \tag{17}$$

$$2F_2 + 2H_2O \longrightarrow H_2F_2 + 2HFO \tag{18}$$

$$2F_2 + 2H_2O \longrightarrow 2H_2F_2 + O_2 \tag{19}$$

$$F_2 + H_2O \longrightarrow H_2 + OF_2 \tag{20}$$

$$F_2 + H_2O_2 \longrightarrow H_2F_2 + O_2 \tag{21}$$

$$OF_2 + H_2O \longrightarrow H_2F_2 + O_2 \tag{22}$$

$$OF_2 + H_2O_2 \longrightarrow H_2F_2 + O_3 \tag{23}$$

$$OF_2 + 2H_2O \longrightarrow H_2F_2 + H_2O_2 \tag{24}$$

$$OF_2 + 2H_2O_2 \longrightarrow H_2O + H_2F_2 + O_2 \tag{25}$$

$$2HFO + H_2O \longrightarrow H_2F_2 + H_2O_2 \tag{26}$$

$$2HFO + H_2O \longrightarrow OF_2 + 2H_2O \tag{27}$$

Recent work would seem to indicate that equations (18), (20), and (23) are the least likely to take place; and, if equation (18) would not take place, then equations (26) and (27) would also be eliminated. However, if (18), (26), and (27) would take place, the resulting products would remain the same as with some of the other equations. Equation (19) is an overall reaction which might involve combinations of (16) and (22); (17) and (21); or (16), (24), and (21). It is known that the products of fluorine in aqueous solutions are oxygen, oxygen fluoride, and hydrogen peroxide in varying amounts depending on the pH of the solutions. After considering the heats of formation of the various compounds, the fact that the explosions seem to take place in the bubbles of fluorine gas, and the known products that are formed, equations (16), (17), and (24) likely take place. The products of these reactions, then, could react in the highly

exothermic reactions (25) and (21) to give off heat and light explosively. They may well react as gases in the bubble of fluorine as it rises in the solution.

G. Peroxides and Superoxides

1. General considerations

The availability of 90% hydrogen peroxide suggested the possibility of using it as a powerful oxidizing agent, even though dilute hydrogen peroxide is reported, by Bancroft and Murphy,[69] to have no action on chlorates and to reduce periodates readily. Bancroft and Murphy also reported that many variable results are obtained using hydrogen peroxide, because the oxidation or reduction ability of hydrogen peroxide depends largely on the pH of the solution. They further postulated that hydrogen peroxide did not give monatomic oxygen as a product of its decomposition, thus hydrogen peroxide was not nearly as good an oxidizing agent as would otherwise be the case. Young,[70] as well as many others, has studied the easy reduction of bromates with hydrogen peroxide in acid solutions. The experiments with 90% and 30% hydrogen peroxide were therefore carried out, in the main, in neutral solutions or with the halate added directly to the hydrogen peroxide. Basic solutions of hydrogen peroxide have a very low oxidation potential, as seen by Table 1, and so were not used extensively in the experiments.

Many authors have reported the formation of periodates by using sodium peroxide; and especially good yields have been obtained by Zintl

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and Morawitz.[48] They heated sodium peroxide with sodium iodide at 400°
to 500° and obtained 98% pure Na_5IO_6. Sodium peroxide and iodine touched
with a red hot point gives local incandescence, and some periodate is
formed.[24] AgO was prepared by the method of Noyes[55] and co-workers, and
used also as a possible oxidizing agent in the anhydrous fused state.
Barium superoxide was prepared from 50% hydrogen peroxide and barium
peroxide by a method described by Baumann[71] which yielded from 10% to 15%
$Ba(O_2)_2$ mixed with barium peroxide. Since the superoxides react rapidly
with water, they were used in the dry state and fused with the halogen
compound.

Potassium superoxide, 96% pure, was fortunately available in small
quantities for a few experiments and used in the nearly anhydrous state.

2. Experiments with hydrogen peroxide

Table 17 contains the data on experiments using hydrogen peroxide of vary-
ing strengths. Violent reactions occurred with 90% hydrogen peroxide
when not kept cold, due to its decomposition and its liberation of more
than enough energy to completely vaporize the remaining moisture. Bromine
was not noticeably liberated from bromates during the reaction with 90%
hydrogen peroxide, though complete reduction to the bromide did occur.
With the iodate, however, there was a strong liberation of iodine as a
purple vapor and as solid iodine in its reaction with 90% hydrogen perox-
ide. Because of the high solubility of hydrogen peroxide in some organic
solvents,[72] some experiments were carried out using them as reaction
mediums. The explosive nature of 90% hydrogen peroxide solutions with

Table 17

Oxidation of Halogens and Halates with Hydrogen Peroxide

Substance	Conc. of H_2O_2	Temp.	Remarks
KIO_4	30%	25^0	all IO_4^- reduced to 95% IO_3^- and 5% I^-
KIO_3	30%	0^0	no change
KIO_3	30%	80^0	40% IO_3^- reduced to I^-, no IO_4^-
$NaIO_3$	30%	25^0	no change
KIO_3 in ether	30%	25^0	no change
$KClO_3$	30%	25^0	no change
$NaBrO_3$	30%	25^0	90% BrO_3^- reduced to Br^-
$KBrO_3$	30%	100^0	95% BrO_3^- reduced to Br^-
I_2 in 6 N KOH	30%	hot	15% IO_3^-, 85% I^-
Br_2 in 6 N KOH	30%	hot	10% BrO_3^-, 90% Br^-
KIO_4	90%	25^0	violent reaction, IO_4^- reduced completely
KIO_3	90%	25^0	violent reaction, I_2 liberated
$KBrO_3$	90%	25^0	violent reaction, 100% reduction to Br^-
$NaClO_3$	90%	25^0	no change
$KClO_3$ solid KOH	90%	0^0	no change
KIO_3 solid KOH	90%	0^0	I_2 liberated, no IO_4^-
$KBrO_3$ solid KOH	90%	0^0	100% reduction to Br^-

organic solvents made its use impractical, and the lower concentrations of hydrogen peroxide gave poor results.

Sodium bromate above 100^0 was treated drop-wise with 90% hydrogen peroxide, but again complete reduction to the bromide resulted.

3. Experiments with solid peroxides and superoxides

Oxidation experiments using metal peroxides and superoxides were carried out in a relatively dry fused state. The heating and fusion was controlled so that complete decomposition did not occur, since this probably would have decomposed any perhalate that might have formed.

Analysis of the residues was difficult due to the presence of excess peroxide. The hydrogen peroxide liberated in aqueous solutions was difficult to remove by boiling and also reduced the periodates that were formed. It was possible to obtain quantitative data on some samples; but, in general, spot tests were used on the dry solids and qualitative data were obtained by examination under the microscope with organic reagents.

Data on this phase of the work are listed in Table 18. The heating was carried out using porcelain boats in a pyrex tube through which ozonized oxygen was passed. The temperature was increased slowly until some reaction could be seen taking place, or until fusion occurred, and held only a short time before cooling. Sparks were commonly given off with the superoxides as the heating took place. The peroxides, in some instances, formed the periodate and perchlorate; but, in general, more decomposition and reduction took place than oxidation. No evidence was found to indicate the formation of any perbromate.

Table 18

Sub-stance	Peroxide	Conditions	Analysis
$NaBrO_3$	Na_2O_2	boiled, aqueous	100% Br^-
$NaIO_3$	Na_2O_2	heated dry[a]	4% IO_4^-
$NaBrO_3$	Na_2O_2	heated dry	Br^- and BrO_3^- present
$NaClO_3$	Na_2O_2	heated dry	no change
Br_2	Na_2O_2	heated dry	Br^- and BrO_3^- present
$NaClO_3$	Ag_2O_2	heated dry	18% ClO_4^-
$NaIO_3$	Ag_2O_2	heated dry	14% IO_4^-
$NaBrO_3$	Ag_2O_2	heated dry	partially decomposed
$NaIO_3$	$Ba(O_2)_2$	heated dry	3% IO_4^-
$NaBrO_3$	$Ba(O_2)_2$	heated dry	partially decomposed
Br_2	$Ba(O_2)_2$	heated dry	Br^- and BrO_3^- present
I_2	$Ba(O_2)_2$	heated dry	I^- and IO_3^- present
$KClO_3$	KO_2	moistened with KOH, heated	no change
KIO_3	KO_2	moistened with KOH, heated	trace IO_4^-
$KBrO_3$	KO_2	moistened with KOH, heated	complete decomposition
$KBrO_3$	KO_2	heated dry	complete decomposition
Br_2	KO_2	heated dry	Br^- and BrO_3^- present

[a]This and the following experiments were carried out by heating the mixtures in a pyrex tube through which ozonized oxygen was being passed.

4. Discussion of results

The hydrogen peroxide experiments indicated an inertness of chlorates towards oxidation or reduction by this reagent under the conditions used in the experiments. Bromates were consistently reduced except in basic solutions, and the iodates were intermediate in their stability towards reduction by hydrogen peroxide. Iodates are formed from iodides in strongly acid solutions by hydrogen peroxide, and they remain stable in strongly basic solutions of hydrogen peroxide, but periodates are reduced easily in both. It was concluded that hydrogen peroxide was not a satisfactory reagent, in any concentration, for the oxidation of the halates to higher oxidation states.

It was somewhat difficult to obtain high yields with the solid peroxides because of the short reaction time which was used. The reaction time was kept short so that the perbromates, if formed, would not decompose upon further heating. As was previously mentioned, high yields of perchlorate have been obtained using silver oxide;[45] high yields of periodate have been obtained using sodium peroxide.[46] The periodates, being relatively stable to heat, allow long reaction times at high temperatures; and even the alkali perchlorates are quite stable toward heat. The bromates, however, and probably the perbromates, are rather easily decomposed by heating.

H. Anodic Oxidation

1. General considerations

If the oxidation potential for the formation of perbromates is too high to be attained chemically, then anodic oxidation could possibly bring about their formation. The formation of perchlorates from chlorates is rather difficult to accomplish chemically even though the oxidation potential is about one volt. The same thing might be true for perbromates; therefore, anodic oxidation might be successful for perbromates as it is for perchlorates.

The main difficulty encountered is in aqueous solutions where the oxidation of water is the major reaction at the anode at high potentials.

Optimum conditions for perchlorate formation have been worked out by a large number of workers.[35,73,74] Electrolysis is carried out, usually with platinum electrodes, in a slightly acid, rather concentrated solution of chloride or chlorate at 25^0 to 50^0, a current density up to 0.6 amperes per square centimeter, and a potential of 6 to 7 volts. Sodium chromate is often used, about three grams per liter, to increase the oxygen over-voltage on the anode. Müller[32] found that sulfate, chloride, chlorate, and fluoride ions all raise the oxygen overvoltage.

Mantell[75] states that materials difficult to oxidize necessitate the use of electrodes with a high oxygen overvoltage and a high current density; also, that oxidation of difficultly oxidizable substances is best carried out in acid solution.

One of the best methods of preparing periodic acid is by the anodic

oxidation of iodic acid using lead dioxide anodes, described by Willard and Ralston.[34] They use a current density of 0.11 amperes per square centimeter.

The electrolytic preparation of bromates is carried out in solutions which are alkaline because of the decomposition of bromates in acid solution. An alkaline solution is then needed when attempting to oxidize bromates to perbromates. Because of the possibility of a catalytic effect and the 99% to 100% current efficiency obtained in making periodates, lead dioxide anodes were used as well as smooth platinum. In order to increase the oxygen overvoltage on the anode, sodium chromate, potassium chromate, and potassium fluoride were used in various experiments. Perphosphates have been formed at the anode in concentrated solutions of potassium fluoride.

Calcium chloride and barium chloride have been used very successfully to obtain 99% yields of perchlorates.[76]

2. Apparatus used

The source of direct current was a Fisher No. 9-261 Electroanalyzer with an output of 0 to 10 volts and a current capacity of 10 amperes at 6 volts.

The anode was a 52 mesh platinum gauge electrode $1\frac{1}{2}$ inches in diameter, 2 inches high, with a weight of 12 grams. Lead dioxide was deposited on this electrode and then used as the anode for some experiments with bromates.

Porous cups were used to contain the anolyte and a stirrer was used to keep the solution from becoming locally acidic. These porous cups were

suspended in the catholyte which was contained in a glass battery jar. The complete cell was then placed in a constant temperature bath.

Another electrode used was a platinum gauze cylinder containing a rotating electrode.

The cathode was a spiral of 12 gauge platinum wire 5 inches long with a weight of 7 grams. A second cathode was a smooth platinum foil with an area of 5 square centimeters.

Anodes were made by mixing graphite or manganese dioxide with sodium silicate and casting the mixture into rods.

3. Experiments with anodic oxidation

Iodates and chlorates were oxidized in slightly alkaline solutions with a smooth platinum anode, and in strongly alkaline potassium fluoride solutions. The electrolysis was continued only until definite yields of both perchlorates and periodates were formed, as determined by qualitative tests. Potassium hydroxide was added to the anolyte to keep the solution always slightly alkaline when bromates were being oxidized.

Two runs were made using warm (50^0) saturated solutions of potassium perchlorate and periodate to which 1 gram of potassium bromate was added. The solutions were cooled gradually during the 10 and 12 hour runs and finally cooled to nearly zero; and the crystallized perchlorate and periodate were analyzed for bromine. The perbromate, if formed, might crystallize with and be stabilized by the isomorphous perhalate present. Bromine was found to be present only in the filtrates, and no evidence of the perbromate was found.

Table 19

Experiments with Anodic Oxidation[a]

Substance	Anolyte	Anode	Time (hrs.)	Temp. $^{\circ}$C.	Approx. c. d.
KIO_3	KOH	Pt	6	40	0.09
KIO_3	KF-KOH	PbO_2	$7\frac{1}{2}$	40	0.1
$NaClO_3$	NaOH	Pt	8	40	0.08
$KClO_3$	KF-KOH	PbO_2	8	40	0.1
$KClO_4$ } $NaBrO$	KF-KOH	Pt	10	50	0.1
KIO_4 } $NaBrO_3$	KF-KOH	Pt	12	50	0.09
$BaBr_2$	KF-KOH	Pt	16	30	0.04
$Ba(BrO_3)_2$	KF-KOH	Pt	16	30	0.05
$KBrO_3$	KF-KOH	MnO_2	22	25	0.06
$KBrO_3$	KF-KOH	MnO_2	20	0	0.06
$KBrO_3$	KF-KOH	graphite	16	40	0.04
$KBrO_3$	KF-KOH	graphite	15	0	0.05
$NaBrO_3$	H_2O	Pt	15	25	0.01
$NaBrO_3$	satd. $NaHCO_3$	Pt	13	25	0.06
$NaBrO_3$	NaOH	PbO_2	24	80	0.05
$KBrO_3$	KF-KOH	PbO_2	20	0	0.04
$KBrO_3$	KF-KOH	Pt	32	25	0.01
$KBrO_3$	KF-KOH	Pt	16	0	0.08
$NaBrO_3$	Na_2CrO_4 in NaOH	Pt	18	30	0.03
$KBrO_3$	K_2CrO_4 in KOH	Pt	19	30	0.04

[a]The catholyte was 2 N nitric acid and varying concentrations of salts, and the voltage was maintained from 3 to 8 volts with an average of 5 to 6 volts.

Some of the attempts to oxidize the halates anodically are listed in Table 19. The temperature, type of electrode, current density, and other conditions were varied. A maximum of 8 volts was used, and with this voltage the discharge of oxygen at the anode was very rapid. The pH of the anolyte decreased rapidly when much oxygen was being discharged. The catholyte volume was large compared to the anolyte, and its pH was nearly constant. Nitric acid was used as the catholyte, and the nitrate ion was reduced to the ammonium ion in the reaction.

Potassium fluoride was used to increase the oxygen overvoltage in the anolyte; and, since sodium fluoride is insoluble, potassium halates were used instead of sodium halates. Weighed quantities of the halates were added to the fluoride bath and allowed to saturate the solution. Concentrated solutions of halates could not be obtained, however, because the fluoride bath was a poor solvent for the sparingly soluble potassium halates.

Both the anolyte and catholyte were stirred rapidly during the electrolysis, and the pH of the anolyte was kept from becoming acidic by adding potassium hydroxide pellets.

The anolyte was removed at the end of each run and diluted to 250 milliliters, from which aliquot portions were analyzed for total oxidizing power by the liberation of iodine and its titration with 0.1 N thiosulfate. An alternate method was also used in which the bromate was reduced with excess standard arsenite and back titrated with 0.1 N iodine solution.

Qualitative tests were employed such as the reactions with silver nitrate, manganous sulfate and phosphoric acid reagent, and organic

precipitants. These were mainly examined under the microscope, and comparisons were made with known solutions which had not been electrolyzed. No evidence of the presence of perbromates was detected.

4. Discussion of results

Latimer[9] lists the following conditions as being necessary for anodic oxidation of perchlorates: first, low temperature; second, neutral or slightly acidic solution; and third, smooth platinum electrodes.

For perbromate formation it was hoped that by using smooth platinum electrodes and a concentrated fluoride bath or the presence of chromates, a high oxygen overvoltage would be obtained. A slightly basic solution was considered necessary for bromates though not as desirable as an acidic solution for oxidation purposes. Low temperatures would permit a higher concentration of atomic oxygen to exist in the solution or on the electrode surface, which should favor oxidation of the bromate. The discharge of oxygen, however, was a decidedly limiting factor under the conditions of the experiments. The voltage was varied in the experiments, but the average voltage was 5 to 6 volts.

As was previously mentioned, perchlorates and periodates were formed in the experiments using chlorates and iodates. Also, the lead dioxide anode gave a better yield of periodate than the smooth platinum. In all of the experiments using bromates, decomposition took place whenever the solution became acidic, or else no change in the bromate took place. All the tests for the detection of a higher oxidation state for bromine were negative.

III. DISCUSSION

The methods by which perbromates might be detected vary with the conditions of each experiment. The ones used in this work are subject to criticism; however, some were definite possibilities under the conditions used. First, if ozone, fluorine, and anodic oxidation of water solutions of isotropic sodium bromate would have produced sodium perbromate, it could have been detected easily under a microscope with polarized light. In these particular solutions no other anisotropic substances would have been present; sodium fluoride is isotropic. Second, perbromates would probably oxidize iodide in acid solutions and thus make the determination of the total oxidizing power significant. The conditions would, of course, require the absence of certain other oxidizing agents. Third, the number of organic reagents that form precipitates or give the same reaction with perchlorates and other ions such as the persulfate, strongly suggests the probability that the perbromate would also give the same reaction to some of those reagents. Fourth, the coprecipitation of potassium perbromate with potassium perchlorate would be easily detected by determining the presence of bromine in the separated perchlorate precipitate.

The bromine atom is large enough to be able to hold covalently three oxygen atoms in bromates and five fluorine atoms in bromine pentafluoride.

This, and a comparison of other similar compounds of elements in other families, leads to the conclusion that perbromates should be capable of existence. The elements of antimony, tellurium, and iodine seem to form compounds with unusually large coordination numbers. This would suggest that the perbromates would have formulae and properties resembling perchlorates rather than periodates.

The likelihood of the perbromate being like the perchlorate is indicated by the difficulty of forming perchlorates by chemical means, whereas the periodates are easily formed.

The stability of the halogen compounds toward heat decreases in the order of iodine to chlorine and to bromine, again suggesting that bromine compounds are nearer to chlorine than to iodine in their properties.

The instability of bromates in acid solutions suggests that the perbromates would also be unstable, despite the unusual stability of perchlorates over chlorates.

Ozone oxidation was inefficient as an oxidizing agent due to the low concentration of ozone and therefore of atomic oxygen. Perhaps if ozone were available in concentrations of 50% to 75% by volume, it would offer more hope as an oxidizing agent for perbromate oxidation.

Peroxydisulfates were strong oxidizing agents when used in conjunction with catalysts such as the silver ion, but in neutral or acid solutions there was a tendency to liberate the free halogen.

The very strongly oxidizing conditions produced in aqueous fluorine solutions should have oxidized bromates to perbromates. This suggests that perbromates are either unstable in aqueous solutions and decompose

before detection, or they are simply unstable and do not form. It seems unreasonable to assume an oxidation potential for the formation of perbromates greater than 2 to 3 volts. If one does even this, anodic oxidation or fluorine oxidation would surely achieve a high enough potential. One must, however, keep in mind the low oxidation potential for the formation of perchlorates, and yet its difficult formation by chemical oxidation.

The extremely easy and complete oxidation of chlorates to perchlorates in the dry state with atomic oxygen, as carried out by Fowler and Grant,[45] and by the writer in the experiments with sodium bromate and potassium chlorate, seems to offer the best hope of success in forming perbromates. Oxidation potentials for aqueous solutions would not necessarily apply to reactions in the dry state. Stability toward heat, of course, is of primary importance. Any objection due to water would be removed and temperatures below the decomposition temperature of potassium and sodium bromate could be used, decreasing the possibility of decomposing the perbromate.

The writer feels it would be profitable to continue the work, using atomic oxygen-giving compounds which decompose at low enough temperatures that the bromate would not decompose. The compound, silver oxide, decomposes at 280°; but it seems to catalytically decompose potassium bromate below its decomposition temperature of 370°. Finding a suitable compound was the main difficulty encountered in the short time available for this phase of the present work. However, lithium chlorate may be one possibility, since it decomposes at about 270°. This compound could be heated

with rubidium bromate whose decomposition temperature is above 430^0.
Lithium chlorate should be a good compound to heat with potassium chlorate
to form the perchlorate. Another possibility is to heat rubidium bromate
with another rubidium salt that would decompose at a low temperature, such
as 200^0 to 300^0.

The experiments performed in this work did not succeed in forming
perbromates; neither did they give evidence to support the conclusion that
perbromates cannot be made.

IV. SUMMARY

1. Methods of oxidation that have been used to prepare perchlorates and periodates, as well as some new methods, were used in attempts to prepare perbromates.

2. These methods included the use of some of the best oxidizing agents known: fluorine, chlorine, ozone, peroxydisulfates, peroxides, superoxides, and anodic oxidation. In some experiments, silver and cobalt catalysts were used.

3. Heating potassium chlorate with sodium bromate gave high yields of perchlorates, so bromates were heated with a number of compounds which decompose and furnish atomic oxygen.

4. Methods of analysis which apply to the other perhalates were used in attempting to detect perbromates.

5. Microscopic examination was made, in many instances, using organic spot test reagents in an attempt to detect the presence of the perbromate ion.

6. No evidence of the formation of perbromates was obtained in any of the experiments conducted.

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