Mixed Perchloric and Sulfuric Acids

I. Simultaneous Oxidizing and Reducing Properties of Hot Concentrated Perchloric Acid

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THE oxidation reactions of hot, concentrated perchloric acid are the basis of important reactions of quantitative analysis (3, 6). The intensity of these oxidations is greatly influenced by the extent to which the acid has been dehydrated. With hot acid of strength greater than that corresponding to the formula O₂H₅ClO₄ (4), simultaneous reducing properties are in evidence. These reducing properties are accounted for if either hydrogen peroxide or ozone is present in traces as a result of the decomposition. Reactions corresponding with this explanation can easily be demonstrated. The acid strength of 70 to 72 per cent perchloric acid is conveniently increased to 85 per cent or higher by the addition of sufficient 96 per cent sulfuric acid or fuming sulfuric acid. For many reactions of analytical importance, these principles require a close study of conditions. It is the purpose of this paper to describe the general aspects of this subject.

Decomposition in Presence and Absence of Mild Reducing Agents

By concentrated perchloric acid, this paper refers to that strength between 70 and 85 per cent $HClO_4$ by weight (roughly, that concentration between dioxonium perchlorate and oxonium perchlorate, $O_2H_5ClO_4$ and OH_3ClO_4). Hot, concentrated perchloric acid decomposes mainly according to reaction 1. A secondary reaction, 2, is also possible to a slight extent.

$$\begin{array}{l} 4\mathrm{HClO}_4 \longrightarrow 2\mathrm{Cl}_2 + 7\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} & (1) \\ 2\mathrm{HClO}_4 \longrightarrow \mathrm{Cl}_2 + 3\mathrm{O}_2 + \mathrm{H}_2\mathrm{O}_2 & (2) \end{array}$$

Both reactions are intensified in proportion as the concentration increases. Reaction 3 indicates the formation of oxonium perchlorate using concentrated or furning sulfuric acid.

$$O_2H_5ClO_4 + H_2SO_4 \longrightarrow OH_3ClO_4 + H_2SO_4$$
 (hydrated) (3)

An important example of a reaction using hot concentrated perchloric acid as an oxidizing agent is the oxidation of trivalent chromium to the hexavalent state in the process of Willard and Gibson (6) for the quantitative estimation of chromium in chromite, ferrochrome, and stainless steel. In a study of this method, Lundell, Hoffman, and Bright (2) state that the oxidation is never quite complete. The following reaction is shown to be quantitative only to the extent of 99.5 per cent completion:

$$Cr_2O_3 + 2HClO_4 \longrightarrow 2CrO_3 + H_2O + Cl_2 + 2O_2$$
 (4)

If chlorine and oxygen are the only decomposition products, it is difficult to offer a reason for this. In the presence of a small amount of hydrogen peroxide the following reaction explains the fact:

$$2\mathrm{CrO}_{3} + 6\mathrm{HClO}_{4} + 3\mathrm{H}_{2}\mathrm{O}_{2} \longrightarrow 2\mathrm{Cr}(\mathrm{ClO}_{4})_{3} + 3\mathrm{O}_{2} + 6\mathrm{H}_{2}\mathrm{O} (5)$$

Reactions 1 and 4 are much more intense than 2 and 5. The difference accounts for the 0.5 per cent reversal of reaction 4. Reactions 2 and 4 are intensified by increasing the strength of perchloric acid. By properly regulating conditions of time, temperature, and acidity, the Willard and Gibson method (6) can be made to give more accurate results, as will be shown in a subsequent paper. The influence of hydrogen peroxide as described may easily be duplicated by the addition of a trace of it to a hot, dilute solution of chromic acid in perchloric acid. The chromium is instantly reduced to green chromic ion.

OXIDATION OF CHROMIC OXIDE TO CHROMIC ACID

Two hundred milligrams of chromic oxide were treated with 50 ml. of oxonium perchlorate (84.79 per cent $HClO_4$) and heated to 168° C. The reaction mixture was allowed to cool. Red crystals of chromic oxide, insoluble in concentrated perchloric acid, formed and the acid was colorless. Upon standing 12 hours at room temperature, the acid became colored owing to the presence of green chromic perchlorate. Repeating the heating of the acid and oxidation of chromium, the results are duplicated (reactions 4 and 5).

The oxidation of chromic oxide was tested with increasing strengths of perchloric acid produced from various proportions of 15 per cent fuming sulfuric acid and 72 per cent perchloric acid (Table I). Parallel experiments were made replacing chromic oxide by small amounts of manganese perchlorate, $Mn(ClO_4)_2$ ·6H₂O. The manganese was momentarily oxidized to permanganate and the reaction rapidly reversed as shown by the immediate decolorization due to hydrogen peroxide formed simultaneously. The reaction is intensified in the presence of a little phosphoric acid.

TABLE I. OXIDATION OF CHROMIUM AND MANGANESE BY CON-CENTRATED PERCHLORIC AND SULFURIC ACIDS

SULFURIC ACID 15 per cent fuming <i>Ml</i> .	$\begin{array}{c} \text{Perchloric} \\ \text{Acid} \\ 72 \text{ per cent} \\ Ml. \end{array}$	TEMPERATURE AFTER MIXING From 25° C. to $^{\circ}$ C.	Cr ₂ O ₃ OXIDATION TO Cr ₂ O ₃ ° C.	Mn ⁺⁺ Oxidation to MnO ₄ ⁻ ° C.
$10 \\ 12 \\ 13.3 \\ 15$	$\begin{smallmatrix}10\\8\\6.6\\5\end{smallmatrix}$	$82.0 \\ 84.4 \\ 86.5 \\ 88.4$	$136 \\ 128 \\ 120 \\ 119$	150 137 128 125
10 (95 %)	10	40.0	168	

The heat attained upon mixing the acids of Table I is an indication of the extent to which the perchloric acid has been dehydrated. By using 75 per cent sulfuric acid, a mixture with 72 per cent perchloric acid results in no appreciable evolution of heat. The temperature after mixing was observed in a 30-ml. Dewar test tube, evacuated but not silvered, and the temperature maximum found using a small Anschütz thermometer.

It will be seen that the dehydration of perchloric acid by the sulfuric acid in all cases was equivalent, at least, to the formation of oxonium perchlorate, since the temperature at which the chromium was oxidized is equal to or less than that required by the 84.79 per cent perchloric acid as previously described. The greater the dehydration of perchloric acid, the lower is the temperature of oxidation. In all cases in Table I the oxidation of chromium was clearly reversed to an obvious extent, as shown by the color change resulting upon allowing the solutions to cool and stand. In the case of the higher concentrations of perchloric acid, the reduction was complete in a few hours. This indicates the magnitude of hydrogen peroxide formation as governed by perchloric acid concentration.

OXIDATION OF TRIVALENT CERIUM TO TETRAVALENT STATE

Solutions of cerous perchlorate in hot, concentrated perchloric acid are not oxidized to ceric perchlorate at 168° to 200° C. Mixtures of equal parts of 96 per cent sulfuric acid and 72 per cent perchloric acid oxidize cerous sulfate readily to ceric sulfate at approximately 140° C. The reaction is as follows:

$$7\text{Ce}_{2}(\text{SO}_{4})_{3} + 2\text{HClO}_{4} + 7\text{H}_{2}\text{SO}_{4} \longrightarrow 14 \text{Ce}(\text{SO}_{4})_{2} + \text{Cl}_{2} + 8\text{H}_{2}\text{O} \quad (6)$$

Ceric sulfate is insoluble in 75 to 95 per cent sulfuric acid and in the reaction mixture of acids outlined above. The substitution of 75 for 96 per cent sulfuric acid is found to result in more complete oxidation of cerium at 185° C. In accordance with the principles previously described, this is accounted for through the practical elimination of hydrogen peroxide as a minor decomposition product of hot, concentrated perchloric acid.

The principle of reaction 6 has been applied to the preparation of ceric sulfate, both in the form of the anhydrous salt and in its addition compounds with ammonium sulfate. The data are included in a subsequent paper. Ceric perchlorate has been prepared in solution by the electrolytic oxidation of cerous perchlorate in a perchloric acid solution by Fichter and Jenny (1). It is possible that a mixture of perchloric and sulfuric acids may be found desirable in the quantitative determination of cerium. A preliminary study has been made with favorable results.

Uses for Mixed Acids in Analytical Studies

The many advantages found in the determination of chromium following perchloric acid oxidation (6) make the method popular in routine plant control analyses. With technical grades of 68 to 70 per cent perchloric acid (free from chromium) the method is less costly. By employing mixtures of per-chloric and sulfuric acids, the method can be cheapened further and at the same time other advantages besides economy in the cost of perchloric acid can be shown.

Mixed perchloric and sulfuric acids have been used satisfactorily in the oxidation of potassium ferro- and ferricyanides to liberate the ferric ion as a standard procedure in the evaluation of titanous solutions. Perchloric acid alone can be used in this case, but the method is cheaper using the mixed acids.

The addition of perchloric acid to 96 per cent sulfuric acid for the destruction of organic matter in the familiar Kjeldahl nitrogen determination has been proposed. Attempts to diminish the time of digestion following this process have proved highly successful. Unfortunately, the process in certain applications gives low results, presumably due to loss of nitrogen in the digestion period. If the concentration of sulfuric acid is lowered to 75 per cent and the 72 per cent perchloric acid is then added to the hot sulfuric acid, the oxidizing power is not materially diminished and there is little tendency toward the formation of hydrogen peroxide as a decomposition product. The change thus proposed may eliminate the disturbing reactions previously mentioned. The problem is being investigated in these laboratories.

The dehydration of silica by hot, concentrated perchloric acid in the method of Willard and Cake (5) has become an important analytical procedure. With a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid, the intensity of the dehydration may be sufficiently high without showing a tendency to convert the perchlorates present to sulfates. Such an application would result in the obvious advantage of economy in cost of perchloric acid where it is applicable. The subject is being investigated.

If the dehydration of perchloric acid by sulfuric acid is objectionable, other methods are available. Anhydrous magnesium perchlorate in various proportions can be dissolved in 72 per cent perchloric acid. Phosphoric anhydride or acetic anhydride may be substituted for the anhydrous magnesium perchlorate.

SIGNIFICANCE OF HYDROGEN PEROXIDE DECOMPOSITION OF PERCHLORIC ACID

It is difficult to demonstrate experimentally the formation of hydrogen peroxide by the decomposition of hot, concentrated perchloric acid according to reaction 2, except by interpretation of the resulting effects as shown. Attempts to distill out hydrogen peroxide at a low temperature by passing air through a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid were not successful. Such an experiment using anhydrous perchloric acid might be more successful. If the decomposition products of hot, concentrated perchloric acid do not include hydrogen peroxide, the reactions obtained are exactly analogous to those that would be obtained if hydrogen peroxide or ozone were formed. The odor of ozone was never apparent. The simultaneous formation of hydrogen peroxide and chlorine as decomposition products would be expected to result in side reactions destroying the hydrogen peroxide.

If hydrogen peroxide can be shown to be formed in the reactions of hot, concentrated perchloric acid, or is conceded to have been shown by the studies of the present series of papers, then perchloric acid must be classified as a true peracid. Present interpretations of the molecular structure of anhydrous perchloric acid and its lower hydrates do not include the assumption of oxygen to oxygen linkages as would be the case if it had true per-acid properties. This question is of far less importance than is the knowledge of the practical influence of the formation of hydrogen peroxide upon the analytical applications.

No violent reactions were encountered in connection with this work.

SUMMARY

Hot, concentrated perchloric acid has been shown to have reducing as well as oxidizing properties. The oxidation reactions result from the decomposition to form chlorine and oxygen. The reducing properties are assumed to result from the simultaneous formation of hydrogen peroxide. An experimental demonstration of its reducing properties has been made.

The reducing reactions of hot, concentrated perchloric acid increase directly with the concentration and temperature. The conditions can be adjusted over a wide range by the use of mixtures of sulfuric acid and perchloric acid and by working at different temperatures. A proper balance between oxidation and reduction relationships can then be obtained.

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