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Notes on the preparation and analysis of halogenide-free
rhodium(III) perchlorate (sulfate) solutions

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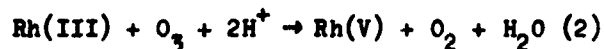
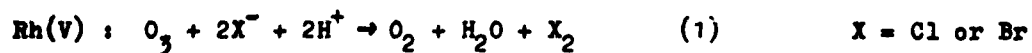
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Abstract

A method is described for the preparation of halogenide-free rhodium(III) perchlorate (sulfate) solutions. As starting material, rhodium chloride or rhodium bromide can be used. The halogenide was removed by means of ozone, which oxidizes "free" (not complex-bound) halogenide to halogen and Rh(III) to



The Rh(V) produced, being a strong oxidizing agent, also reacts with the halogenide according to $\text{Rh(V)} + 2\text{X}^- \rightarrow \text{Rh(III)} + \text{X}_2$ (3)

Methods for the detection of halogenide-ions in rhodium solutions are given.

Notes on the preparation and analysis of halogenide-free rhodium(III) perchlorate (sulfate) solutions.

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Problem

* For studies on the hydrolysis and other reactions of rhodium(III) and rhodium-ions of higher oxidation states, it was desired to prepare rhodium(III) perchlorate and sulfate solutions that were free from detectable amounts of halogen ions. As is well known, the halides¹ form strong complexes with rhodium(III) and also with rhodium of higher oxidation states. Moreover, it is known^{2,3}, and was confirmed in the present work, that the formation and breakdown of the halogeno rhodium complexes is a rather slow process. Hence, in a solution containing appreciable amounts of halogenide, one may expect a very slow establishment of also other equilibria.

In preliminary experiments, methods proposed by previous authors^{4a,4b,5,6,7a,7b} proved to give unsatisfactory results - in general, the solutions still contained halogenide (for analysis methods, see end of report). Moreover, none of these methods seems to be practical for the preparation of a substantial amount of relatively concentrated perchlorate solution.

It has, however, proved possible to develop a new method which seems to give rhodium solutions that are sufficiently free from halogenide ions and therefore suitable as a starting material for studies concerning this element.

Starting material: chloride or bromide

As starting material in all the initial experiments, solid $\text{RhCl}_3(\text{H}_2\text{O})_4$ of a purity higher than 99.7 % (delivered by A.D. MacKay, Inc.) was used.

Alkali or sulfate ions could not be detected in the preparation.

Later on, a rhodium bromide solution (stoichiometric composition undetermined) was found to be a still more convenient starting material.

$\text{RhBr}_3(\text{H}_2\text{O})$ was first prepared from its components by Goloubkin in 1910^{8a,8b}. Spongy Rh (1 g) was sealed in a tube with 24 g 40 % HBr and 7 g and kept Br_2 at 80-100°C for 48 h. We found, however, that a simpler procedure gave equally good results: finely divided rhodium metal was found to dissolve in the mixture of HBr + Br_2 if it was refluxed on a water bath for 24 h. After the metal had dissolved, the excess of reagents was distilled off under reduced pressure. The dry residue was redissolved in water and once more evaporated to dryness. The substance obtained had a deep brown color with a tinge of violet and was completely soluble in water.

This method of synthesis is very convenient and we now feel that rhodium bromide prepared in this way is preferable to rhodium chloride as the first step in the preparation of rhodium solutions. The method has the added advantage that one can use rhodium metal residues from the classical gravimetric rhodium determination according to Gilchrist and Wichers (sulfide $\rightarrow$ oxide $\rightarrow$ reduction in H_2 atmosphere at about 450°C) and also rhodium recovered from various waste solutions by reduction with hydrazine or hydrogen, washing, igniting and reducing it again.

Preparation of perchlorate (sulfate) from halogenide: experience with older methods

Rhodium does not dissolve directly in HClO_4 . On the other hand, the metal may be brought slowly into solution by boiling with a large excess of conc. sulfuric acid or by fusion with potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$). These methods of dissolution have - for our purposes - a theoretical interest only. They require the introduction of an immense excess of the reagent which cannot be easily removed.

Thus, in order to prepare a rhodium perchlorate (sulfate) solution, it is necessary to start with a soluble salt.

The following methods employing $\text{RhCl}_3(\text{H}_2\text{O})_4$ may be found in the literature.

1. According to Grube^{4a,4b}, the rhodium(III) hydroxide can be precipitated, washed, and dissolved in $\text{HClO}_4(\text{H}_2\text{SO}_4)$, under suitable conditions.
2. Recently, Shukla^{7a,7b} proposed removing the chloride by adding AgClO_4 .
3. Jørgensen⁵, and Ayres and Forrester⁶ recommended evaporation with excess $\text{HClO}_4(\text{H}_2\text{SO}_4)$.

In addition, one might suggest

4. Passing a rhodium(III) chloride solution through a ClO_4^- or SO_4^{2-} -saturated anion exchanger.

Attempts were made to use Grube's method but it was soon found that the resulting solutions always contained considerable amounts of chloride. Since the final Cl^- content is much influenced by the experimental conditions chosen, the procedure will be briefly described. A dilute solution of $\text{RhCl}_3(\text{H}_2\text{O})_4$ (2 g/l) in distilled water was prepared, filtered, and then kept nearly boiling for at least one hour in order to destroy, as far as possible, the chloro-rhodium complexes. To the hot solution, strong NaOH was added till the pH was around 9 (as measured by spot test on an indicator paper). By that time, some of the rhodium had again dissolved as hydroxo complexes. The acidity was then adjusted with HClO_4 until all rhodium was precipitated as rhodium(III) hydroxide.

The rhodium(III) hydroxide may also be precipitated using Na_2CO_3 solution, the solution being first made alkaline to pH 9. The precipitation seems to be complete after acidification to $\text{pH} \sim 7^3$. The pH of the colorless supernatant liquid was between 5.7 and 6.

The precipitate was repeatedly centrifuged and washed until no Cl^- could be detected in the washings. Finally, it was dissolved in cold conc. HClO_4 or conc. H_2SO_4 .

It was found, however, that the resulting solutions were not free from Cl^- . Even if the procedure was carried out twice, there remained about 0.16 Cl^- per Rh. It is believed that the Cl^- is retained in the precipitate, perhaps in the form of a hydroxide-chloride. This agrees with the fact that previous investigators also found some evidence for the formation of rhodium(III) hydroxide chloride¹⁰ and hydroxide bromide^{8a,8b} under similar experimental conditions.

Preliminary experience with methods 2,3 and 4 indicated that they were not well suited for the preparation of a substantial amount of relatively concentrated rhodium perchlorate (sulfate) solution. Moreover, none of the methods gave a product free from Cl^- . Details about our experience with methods 2,3 and 4 will be given in a following technical note.

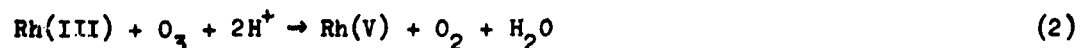
Since none of the methods, nor the anion exchange method, gave satisfactory results, it was considered best to develop a new method. The greatest difficulty seems to be the stability of the halogeno rhodium complexes - only those methods could be considered which do not involve the introduction of substances that are undesirable and hard to remove.

The ozone method

The method presented here is based on preliminary experiments made by this author with the intention of devising a procedure for transforming rhodium(III) into higher oxidation states by means of ozone, O_3 . The reaction of ozone with solutions of rhodium and other platinum metals will be the subject of a forthcoming publication.

Whenever "chloride" is mentioned in the following, the statements are equally true for bromide. In a preliminary experiment, solid $\text{RhCl}_3(\text{H}_2\text{O})_4$ was dissolved in water ($[\text{Rh}] \sim 10 \text{ mM}$, $[\text{H}^+] \sim 10 \text{ mM}$). The solution was cooled to 0°C and ozone passed through it. Only negligible amounts of chlorine were evolved. It was found however that, if the solution had been boiled for a while before ozonizing, chlorine was then given off much faster and moreover rhodium(III),

which is orange-yellow, was partly oxidized to a green species. Studies in progress gave evidence that this species is rhodium(V), so the reactions are:



Yeatts and Taube¹¹ recently studied the kinetics of reaction (1). They found that the rate of oxidation is considerable at 0°C but that it is much slower than the oxidation of bromide¹². In the following, all experiments were carried out on solutions that had been kept nearly boiling for at least one hour in order to break up the chloro complexes.

When solutions of Rh with concentrations between 0.05 and 0.3 M and $[\text{H}^+] \gtrsim 0.2$ M were ozonized, chlorine was evolved for a while at a continually diminishing rate. The solution rapidly turned green because of reaction (2). When no Cl_2 could be detected in the outflowing gas (absorption in NaOH, acidifying and adding Ag^+), the solution was again put on the water bath. Chlorine was again given off, presumably because of the reaction:



The solution slowly turned greenish-brown due to the Rh(III). When the formation of Cl_2 had ceased, the solution was again cooled and ozonized at 0°C - once again, a strong evolution of Cl_2 was observed.

These experiments indicate that the oxidation of free Cl^- is rapid whereas the rate of reaction between ozone and Cl^- bound in Rh complexes is practically negligible.

It is possible to remove all the chloride from a rhodium chloride solution by alternately heating and ozonizing in the cold. This process is, however, rather time-consuming because, under these experimental conditions, the rate of dissociation of the complexes and the oxidation of Rh(III) are rather slow.

It was found that, by lowering the acidity, one could increase the rate of reaction (2) considerably. It seems that, at lower pH values, reaction (2) reaches an equilibrium state when only a part of the Rh has been transformed

to Rh(V). At low acidities, a larger fraction of Rh(V) is obtained and it seems that the redox potential of the Rh(V)/Rh(III) couple is increased so that reaction (3) - especially at higher temperature - gives a higher yield. It should be added that Rh(V) presumably forms weaker chloro complexes than Rh(III).

In developing a final procedure for removing Cl^- with the ozone method, it is necessary to make certain that the chloro complexes are broken up as much as possible. This is favored by 1) dilution, 2) increasing the temperature, 3) decreasing the acidity, 4) oxidizing Rh(III) to Rh(V). It is, of course, also important for the following equilibrium studies that no other foreign substance, except for some Na^+ and the anion desired, is introduced into the final solution.

Method of preparation

Rhodium chloride is dissolved in distilled water to a concentration of about 10 mM. The solution is kept at 90-100°C for 1 h and then 5 M NaOH is added until a pH ~ 8 to 9 is attained. At this pH, the rhodium is partly present as a soluble hydroxo complex. Then, concentrated perchloric acid (or conc. sulfuric acid) is added dropwise until the pH is about 5.7 to 6. At this value, the rhodium is practically completely precipitated.

The precipitate is decanted, centrifuged, washed with hot water and centrifuged again, after which it is dissolved in a minimum of cool concentrated HClO_4 or H_2SO_4 . In this first step, about 90 % of the Cl^- is removed.

The solution is diluted to $[\text{Rh}] \sim 10$ mM, kept on a water bath for 1 h and then ozonized at 0°C and pH ~ 1. When the evolution of Cl_2 has practically ceased, NaOH is added to the solution (still in the ozonizing apparatus) until the pH is 5 or 6. The color then changes very rapidly to dark green due to rhodium(V).

The solution is now acidified to pH 1 or 2 and kept almost boiling: chlorine is evolved vigorously. The solution is then tested for Cl^- (see below). The ozonization at pH 6 and 0°C and the heating at pH 1 are repeated until the

test becomes negative. When the product is satisfactory (usually two cycles suffice), the rhodium(III or V) is precipitated as hydroxide as before, dissolved in the desired amount of conc. acid and, finally, the rhodium(V) is reduced with H_2O_2 .

The method was first worked out for chloride, on which most experiments have been made. It has been found, however, that bromide is preferable since the reaction (3) is much more rapid with Br^- than with Cl^- .

Detection of halogenide ions

The common test for Cl^- using Ag^+ is not reliable in solutions containing rhodium since the main part of the Cl^- is bound to Rh as complex species and does not react with Ag^+ ². Moreover, in dilute solutions that do not contain any halogenide, a light pink precipitate had been observed which contains both Ag and Rh.

In sulfate solutions, the test for halogenide is very simple. Rhodium can be reduced to the metallic state from an acid solution if H_2 is bubbled through at 60-70°C in the presence of a Pt-foil or wire which seems to catalyze the reduction. After the metal has been separated by centrifuging, the halogenide can of course be detected with Ag^+ .

In the presence of perchlorate ions, this method is no longer reliable since some ClO_4^- is reduced to Cl^- , probably due to the catalyzing influence of the finely divided Rh(s). Nor was it practical to remove Rh by reduction to metal with hydrazine in alkaline solution since, in this case, some ClO_4^- was also reduced to Cl^- .

With perchlorate solutions, it seemed unavoidable to precipitate rhodium(III or III + V) hydroxide with NaOH, to separate the precipitate by centrifuging and to test both the precipitate and the supernatant liquid (which is free from Rh) for Cl^- . It is necessary to be rather careful with the pH. If the pH is adjusted to about 5.7 after the precipitation, then the

formation of colloidal rhodium(III) hydroxide, which makes the detection of AgCl difficult, seems to be avoided. Heating is also helpful for coagulating the colloid.

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