[Contribution from the Department of Chemistry of Washington and Lee University]

CONTRIBUTIONS TO THE STUDY OF RUTHENIUM
IX. SOLUBILITY OF RUTHENIUM IN HYPOCHLORITE SOLUTIONS AND AN ATTEMPT TO UTILIZE THE REACTION FOR THE QUANTITATIVE DETERMINATION OF THE METAL

By Jas. Lewis Howe and Frederick N. Mercer[1]

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The first mention of the solubility of ruthenium in solutions of hypochlorites seems to have been by Schönbein,[2] although in 1859 Claus[3] had shown that ruthenium is volatilized as RuO_4 when it is fused with caustic alkalies and the solution of the melt treated with chlorine. Here a somewhat similar reaction is involved, but Claus does not seem to have noted that chlorine has any action on ruthenium suspended in a solution of caustic alkali. The Claus method of purifying the metal is the one that has been all but invariably followed by workers since his time. This consists in fusing the metal, or compounds or mixtures containing the metal, with caustic alkali and some oxidizing agent, this resulting in the formation of potassium ruthenate, K_2RuO_4. The melt is dissolved in water and subjected to a stream of chlorine, ruthenium tetroxide, RuO_4, being formed; this is distilled. As an oxidizing agent, Claus used potassium nitrate, as well as potassium chlorate; of late, sodium peroxide has frequently been used; while more recently Gutbier has used potassium permanganate, which was also used by Howe in his first work. Air can also be used, but its action is relatively slow. When osmium has been previously removed, the ruthenium tetroxide is uncontaminated by any other metal, unless indeed *eka*manganese should be present and form a volatile higher oxide.[4]

While this process of purifying ruthenium has been in general use for more than 60 years, it does not seem to have been subjected to any critical study, and the same is true of the solubility of ruthenium in hypo-

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[1] This paper is based upon the thesis presented by Frederick N. Mercer to the Faculty of Washington and Lee University in partial fulfilment of the requirements for the degree of Bachelor of Science, June, 1925.

[2] Schönbein, *Ann. chim. phys.*, [4] **7**, 103; **8**, 465 (1866).

[3] Claus, (a) *Bull. acad. sci. St. Petersburg*, **1**, 97 (1860); (b) *Mélanges phys. chim. acad. sci. St. Petersburg*, **4**, 20 (1860).

[4] Some years ago, in a long series of purifications of ruthenium, with this in mind, the portions most difficultly precipitable by alcoholic potassium hydroxide were collected and purified. The metal obtained, in all a few milligrams, showed certain reactions, seemingly not characteristic of ruthenium. Dr. W. J. Humphreys, then at the University of Virginia, was kind enough to make several spectrograms of this residue with the Rowland grating at the University; no lines were found which indicated the presence of any unknown element.

chlorite solutions, though such solutions have long been used in this Laboratory and probably others for cleaning apparatus on which ruthenium has been precipitated. It also seemed worth while to investigate the extent to which these reactions could be used in quantitative separations. The study is divided into three parts: solution of ruthenium, conversion into the tetroxide and treatment of the tetroxide when formed.

Solution of Ruthenium.—The conversion of ruthenium into the ruthenate by fusion with caustic alkali and an oxidizing agent has been very fully described in many papers and texts. Which alkali and what oxidizing agent is used depends on the experience of the worker. In this Laboratory sodium hydroxide is generally used, with sodium peroxide, the fusion being carried on in a nickel dish, although formerly potassium permanganate and later potassium nitrate were used.

The solutions of ruthenates are very variable in their stability, even when a large excess of alkali is present. Concentrated solutions generally give an iridescent skin of black ruthenium oxide (supposed to be $Ru_2O_3.Aq$) on the surface of the solution and on the side of the beaker on standing overnight, while more dilute solutions will at times stand indefinitely long without sign of decomposition. Heating dilute solutions does not seem to affect their stability, as dilute solutions were repeatedly boiled without decomposition.

The action of hypochlorites was tested by allowing ruthenium in various forms to stand under solutions of hypochlorites of different strengths in test-tubes. The following will serve as examples of the experiments performed.

Series C.—Three hundred cc. of a solution containing 60 g. of sodium hydroxide was saturated with chlorine gas, the solution being kept cold during the process. To one half of the solution about 5 g. of sodium hydroxide was added, and parts of both solutions were diluted 1:1 and 1:3. The original solution contained theoretically about 200 g. of sodium hypochlorite per liter, and the two dilutions 100 g. and 50 g., respectively. Naturally this amount would be lessened by formation of more or less chlorate. With these solutions were tested: (1) metallic ruthenium in a finely divided form (residues from analyses, in which the ruthenium had been reduced in hydrogen); (2) pure potassium aquo-chlororuthenate, $K_2Ru(H_2O)Cl_5$; (3) rich ruthenium residues as metal, containing considerable quantities of the other platinum metals, except osmium. Small portions of these samples were placed in test-tubes and about 10cc. quantities of the solutions indicated above added, the tubes being shaken from time to time. The results are given in Table I.

The solutions with slight excess of alkali were stable for a considerable time, but after several weeks began to break down, giving a deposit of the black oxide; when, however, a little fresh alkaline hypochlorite was added, the oxide slowly disappeared, giving a clear, orange-red solution. The term "mirror" in the experiments described in Table I is given to the black, mirror-like deposit on the side of the test-tube, immediately

TABLE I

SOLUBILITY OF RUTHENIUM IN SODIUM HYPOCHLORITE SOLUTION

NaOCl soln. G. per liter	Metallic Ru (all dissolved)		Aquo salt (all dissolved)		Ru residues (partly soluble)	
	Soln.	Mirror	Soln.	Mirror	Soln.	Mirror
200	Clear, colorless	Strong	Orange-red	Strong	Orange-yellow	Good
100	Sl. yellow	Less strong	Orange-yellow	Good	Faintly yellow	Fair
50	Markedly yellow	Less strong	Yellow	Weaker	Appr. colorless[b]	Faint
NaOCl + NaOH						
200	Orange	None	Orange-red	None	Orange-red	None
100	Orange	None	Orange-red	None	Orange-yellow	None
50	Lighter orange[a]	None	Orange-yellow	None	Paler	None

[a] Slight undissolved residue. [b] Only slightly soluble.

above the solution, formed by the decomposition of evolved tetroxide; it probably consists of a more or less hydrated oxide, perhaps Ru_2O_3. This mirror always forms when the tetroxide is for a considerable time in contact with glass or porcelain, and is generally insoluble in acids; it usually, but not always, dissolves easily in alkaline hypochlorite solution. It is similar to the decomposition product from ruthenate solutions, and its composition is variable. In all cases when no excess of alkali was present the characteristic odor of ruthenium tetroxide was easily recognized.

Experiments were tried on mixed residues by submitting them to several extractions, and it was found that two, or at most three extractions with the concentrated alkaline hypochlorite solutions served to remove completely all the ruthenium present. It was also found that sodium hypochlorite was more effective than potassium hypochlorite in bringing about solution and for similar strengths was more rapid in its action.

From these experiments the conclusions are drawn that ruthenium, when finely divided, is rather readily soluble in concentrated alkaline solutions of hypochlorites; that it may in general in its compounds be separated quantitatively from all the other platinum metals except osmium; that sodium hypochlorite is more effective than potassium hypochlorite; that when free alkali is present, alkali ruthenate is formed and all the ruthenium is retained in solution; that when little or no alkali is present, more or less ruthenium tetroxide is formed and is slowly given off from the solution, but considerable ruthenium may be retained as ruthenate.

Apparently the first action of the hypochlorite is the direct oxidation of the ruthenium to the tetroxide, and as fast as this is formed it is decomposed by any free caustic alkali present, to the ruthenate.

Distillation of Ruthenium as Tetroxide.—An attempt was first made to distil the ruthenium as tetroxide from the solution in which it had been formed by the action of hypochlorites, and in fact in most cases quite a little passed off as the solution was boiled, but the proportion to that present was small, most of the tetroxide appearing to be decomposed in the solution. From the hypochlorite solutions containing an excess of alkali, no ruthenium tetroxide distils, the ruthenium being wholly in the form of ruthenate.

When an alkaline hypochlorite solution of ruthenium is placed in a retort and subjected to a stream of chlorine, the tetroxide is at once formed and can be distilled, but it was found that in order to remove the ruthenium completely a considerable excess of hypochlorite must be present. When the ruthenium is not completely removed by the first distillation in chlorine, more alkali is added and chlorine admitted, whereupon all the ruthenium can be distilled. When the deep orange-red solution of potassium ruthenate, containing a considerable excess of alkali, is treated with chlorine, no change is evident as long as free alkali is present; but when all of the latter has been converted into hypochlorite, the solution loses its color, and if much ruthenium is present, golden-yellow, oily drops of the tetroxide appear floating on the surface of the liquid. The chlorine stream can then be shut off and the tetroxide distilled. We could usually remove all the ruthenium in a single distillation, but when there was any doubt about all having passed over, the retort was cooled, opened, a few drops of concentrated alkali were added, chlorine was led in and the distillation repeated.

In using this method for the separation of ruthenium from other metals of the platinum group, the metals in the form of finely divided residues were placed in the retort, a solution of concd. sodium hypochlorite (see p. 2927) added, and the whole allowed to stand during occasional agitation for a day. Chlorine was then led into the cold solution until the color changed from deep orange-red to pale yellow, when heat was rapidly applied and the tetroxide distilled. The completeness of the reaction depends upon the state of division of the metal or compounds used. In a few cases a second or even a third treatment was necessary. It is desirable that the solution into which the chlorine is led be cold, in order to avoid formation of chlorate at the expense of hypochlorite.

In our earlier work two difficulties prevented complete removal of all of the ruthenium. One, just noted, arose from having the alkali warm when the chlorine was led in. The other was caused by contamination of the chlorine with hydrochloric acid from the wash bottle. The acid neutralized the alkali and, of course, inhibited the reaction. We later used chlorine from a high pressure cylinder, and had no further difficulty from this source.

When osmium is present, it must be completely removed by distillation with nitric acid before an attempt is made to separate the ruthenium, as osmium, under these conditions, goes with the ruthenium. Most of the material with which we worked was free from osmium. No evidence of the formation of the per-ruthenate, as an intermediate product of the action of chlorine on the ruthenate, was noted.

Treatment of Ruthenium Tetroxide.—The collection of the tetroxide may be accomplished by several methods, according to the use to which the material is to be put. The methods of collecting the pure tetroxide have been described by Gutbier,[5] Krauss[6] and Aoyama.[7] When the ruthenium is to be used as a halogen compound, the tetroxide is collected in hydrochloric or other halogen acid. In neither of these cases is the condensation or absorption of the oxide quantitative, as even in a very cold receiver some of the very volatile tetroxide escapes, nor do these methods lend themselves to quantitative determination. If alcohol has been added to the acid, the tetroxide is reduced more completely, and partly converted into the aquo pentachlororuthenic acid, $H_2Ru(H_2O)Cl_5$.

When the ruthenium tetroxide is received in cold alkali, such as potassium hydroxide, it reacts rather rapidly forming potassium ruthenate, K_2RuO_4, or possibly at times potassium per-ruthenate, $KRuO_4$, which is, however, unstable. With a cold receiver it is possible to condense all of the ruthenium in potassium hydroxide without loss. When alcohol is added to the solution of potassium ruthenate it is at once decomposed with the formation of a black hydrated oxide (probably Ru_2O_3. Aq.), which dissolves readily in hydrochloric acid to form pentachlororuthenic acid, H_2RuCl_5. A more convenient way to collect the ruthenium is to distil the tetroxide directly from the retort into a solution of dil. alcoholic potassium hydroxide. We have once or twice had slight explosions of the vapors in the retort from contact with the alcohol, but usually there has been no trouble, possibly owing to the dilution of the vapors with steam or chlorine or both.[8]

We found no difficulty in precipitating the ruthenium completely by leading the vapor from the retort into cold alcoholic potassium hydroxide but care must be taken that no considerable quantity of chlorine passes over with the tetroxide. If much chlorine is taken up by the alcoholic potassium hydroxide, the precipitated black oxide forms a colloidal solution and fails to settle; nor was it found possible to separate it save by evaporating nearly or quite to dryness. For this reason we stopped the stream of chlorine as soon as the change of color of the solution in the retort indicated that all the ruthenium had been changed from ruthenate to the tetroxide. In our first work the tetroxide was received in closed vessels, but later we found no difficulty, when working with small quantities of ruthenium,

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[5] Gutbier, *Z. angew. Chem.*, **22**, 487 (1909).

[6] Krauss, *Z. anorg. Chem.*, **131**, 348 (1923).

[7] Aoyama, *ibid.*, **138**, 249 (1924).

[8] Ruthenium tetroxide appears to be very erratic with regard to stability; both Deville and Debray and Gutbier had violent explosions when distilling it, yet at times it has been distilled without danger. Claus (Ref. 3 b, p. 23), who first worked with it, speaks of precipitating it with alcohol and of drying it on filter paper, and makes no mention of explosions; while one of us [Howe, *Chem. News*, **78**, 269 (1898)] had a severe explosion caused by alcoholic potassium hydroxide sucking back into a receiver containing a small quantity of liquid tetroxide, and observed that when small drops of the tetroxide fell upon wood, paper, or other organic material, these at once burst into flame. It is possible that this aberrancy may be accounted for by the observation of Krauss (Ref. 6) that the tetroxide exists in two modifications.

in recovering it completely, by having the (bent) end of the retort dip into an open beaker containing dil. alcoholic potassium hydroxide.

After the distillation was ended, gentle warming of the beaker caused the black oxide to settle, leaving above a clear, colorless solution, containing no trace of ruthenium. Here, however, the success of our work from the standpoint of quantitative determination ceased. No satisfactory method could be found to collect this oxide for weighing, or for the preparation of alkali-free solutions, as it is impossible to free it from the alkali present. It is easily collected on a filter paper, but after a single washing it begins to pass through the filter in colloidal form. We attempted to get the ruthenium in a pure condition by burning the partially washed and dried precipitate, after moistening it with a few drops of dil. hydrochloric acid (otherwise the alkali present formed a trace of ruthenate when the mixture was heated), reducing in hydrogen, then washing the ruthenium thoroughly with boiling water, filtering again, burning and again reducing in hydrogen. The method is too complicated for quantitative work, and we succeeded in recovering in three experiments only 93.35, 97.93 and 94.07% of the 0.0617, 0.0968 and 0.0658 g. of metallic ruthenium used.[9]

It is also possible to obtain the ruthenium by dissolving the precipitate of black oxide, from which the supernatant liquid has been decanted, in hydrochloric acid, precipitating with *an excess* of zinc dust, dissolving the excess of zinc in hydrochloric acid, filtering off the ruthenium, burning and reducing in hydrogen. This is also unsatisfactory from the standpoint of quantitative analysis. What is needed at this point is a satisfactory volumetric process, but none has yet been proposed.

A number of precipitants other than alcohol were tried with the potassium ruthenate solution. *iso*Propyl, *n*-butyl and *iso*butyl and benzyl alcohols gave complete precipitations, as well as acetone and chloroform; methanol, amyl alcohol and toluene gave incomplete precipitations, with a tendency to form colloidal solutions and the precipitation with glycerol was also incomplete. No precipitant was found more satisfactory than ethyl alcohol.

Summary

1. When finely divided,[10] ruthenium and its compounds are completely

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[9] Mr. Mercer is of the opinion that after sufficient experience with the method it should be possible to effect a complete recovery of the ruthenium present. (J. L. H.)

[10] Since the above was written, Dr. Raleigh Gilchrist of the Bureau of Standards has called my attention to the difficulty of dissolving ruthenium in hypochlorite solution, when it is in the form of crystalline powder, the form in which it often comes on the market. Solution of this form can be effected, but it requires prolonged digestion and frequent renewal of the solution, and is promoted by agitation. On the other hand, when in *finely divided* condition, as specified in the paper, it dissolves readily.

soluble in solutions of alkali hypochlorites. When an excess of alkali is present, ruthenates are formed; when no excess of alkali is present, some ruthenium tetroxide is formed.

2. When finely divided, ruthenium can be completely separated from the other platinum metals, except osmium, by solution in hypochlorites.

3. From a solution of potassium ruthenate, ruthenium can be completely distilled as tetroxide, after treatment with chlorine.

4. No satisfactory way has been found to precipitate quantitatively in weighable form the ruthenium from the tetroxide.

Lexington, Virginia

NOTE

An Attempt to Excite a Mercury Surface by Electron Bombardment.— The present results on chemical effects incident to the electron bombardment of a mercury surface are tentative in the sense that they lead to no clear-cut interpretation, but since it is impossible to continue the work in the immediate future it is deemed best to publish the observations made.

The method adopted to detect excitation of the surface was very simple in principle. Potentials of 0–240 volts were impressed between a hot-wire filament and a mercury surface in an apparatus similar to that used by Moore and Noyes[1] in their investigation of the relation of photoelectric effect to photochemical action on mercury. This reaction vessel was evacuated to pressures of 10^{-4} to 10^{-5} mm. and oxygen gas admitted a fraction of a second before the filament current was turned off in the hope that the presence of excited mercury atoms could be detected by formation of oxide. Filaments (tungsten, thoriated tungsten, platinum and oxide-coated platinum were tried in separate experiments) were mounted 5–7 cm. from the surface of area approximately equal to 0.75 sq. cm. This distance is considerably less than the mean free path of electrons at the pressures used.

A distinct indentation, or crinkling, of the surface was always found to occur when oxygen at pressures ranging from 7–30 cm. was admitted suddenly before the filament current was switched off. Moreover, this effect was found to persist when the gas was admitted at times as long as five minutes after turning off the filament current. Evidently this "long-time" effect is scarcely anticipated by the assumption that the duration of excitation of surface atoms of a solid is of the same order as that of a gas. In every case, however, it was noticed that when the excess of oxygen was pumped out after a run this extremely tenuous

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[1] Moore and Noyes, This Journal, 46, 1371 (1924).