

The Reduction of Ruthenium Tetrachloride

by

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Stannous Chloride.

Claus, in his early work, described two classes of ruthenium chloride,  $\text{Ru}^{\text{III}} \text{Cl}_3 \cdot 2 \text{HCl}$  and  $\text{Ru}^{\text{IV}} \text{Cl}_4 \cdot 2 \text{HCl}$ ; the former made by the action of hydrochloric acid upon any of the soluble oxides or hydrated oxides and the latter, generally at least, by the oxidation with nitric acid. The trichloride is also formed when chlorine acts directly on the metal, especially in the presence of alkaline chlorides.

In addition to these chlorides, Claus called attention to the fact that by the action of hydrogen sulfide, the deep red-brown solution of ruthenium trichloride becomes dark azure-blue, probably owing to the reduction to a bichloride,  $\text{Ru}^{\text{II}} \text{Cl}_2$ . No further advance was made on the chloride until Joly showed that the chloride obtained by oxidation with nitric acid is not as Claus had supposed tetrachloride, but a nitrosochloride,  $\text{Ru Cl}_3 \text{NO}$ . More recently Antony has shown that by adding potassium ruthenate,  $\text{K}_2 \text{Ru O}_4$  to hydrochloric acid, the true tetrachloride,  $\text{Ru}^{\text{IV}} \text{Cl}_4 \cdot 2 \text{HCl}$  is really formed, and it appears quite possible that Claus may have had this salt in hand, and in one case have analyzed it. He did not, at all events, distinguish it from the nitrosochloride. Joly also studied the azure-blue solution of the reduced

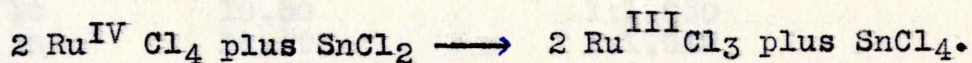
chloride and concluded that it contains an oxychloride,  $\text{Ru Cl}_2 \text{OH}$ . Joly in his work passed a mixture of chlorine and carbon monoxide over finally divided ruthenium at a comparatively low temperature. A very voluminous powder was obtained which contained anhydrous trichloride. This is insoluble in water, acids, and strong alcohol, to the same dark azure-blue solution. On distilling this in vacuum he obtained what he considered to be the oxychloride, and he looked upon the blue solution as  $\text{Ru (OH) Cl}_2$ . Inasmuch as in the solution of this variety of the trichloride, aldehyde is formed, and since the blue color is produced in every case by a reducing action Howe thought it probable that a true bichloride was present. He did not succeed though in preparing a pure salt from the blue solution, but several were prepared point to a compound of the formula  $3\text{CsCl}, 2\text{Ru Cl}_2 \cdot 2\text{H}_2 \text{O}$ . These were formed by reducing a solution of ruthenium trichloride in an electrolytic cell, and immediately adding cesium or rubidium chloride. The fine precipitate varies from dark greenish-blue to olive green, and oxidizes with great rapidity. In analyses of this compound the amount of chlorine is *usually too large in proportion to* the ruthenium to be  $\text{Ru Cl}_2$  but always too small to be  $\text{Ru Cl}_3$ . The investigations upon the blue solution are

still being carried on. I wish to touch on this reaction as I ran across it several times in my reduction of ruthenium tetrachloride to the trichloride with stannous chloride. If the salt is not completely in solution a fugitive greenish-blue solution is produced, which turns azure blue-blue on standing a short while and then returns to the yellow of the trichloride on further standing.

Joly and Howe, tried in vain, various methods of chlorination to form the tetrachloride from the trichloride but apparently  $\text{Ru Cl}_3$  will not take up another chlorine. Antony first prepared the chloride, using potassium chlorate to oxidize the ruthenium to ruthenate, thus insuring the absence of a nitrate and hence nitrosochloride formation. The solution of the ruthenate was then added to dilute hydrochloric acid. On the other hand, when acid is added to ruthenate, even at a temperature below zero, and the solution concentrated in the cold, the trichloride was the only product obtained. The solution of the trichloride and the tetrachloride so closely resemble each other that the study of their formation is enhanced in difficulty. Howe as yet has noted but a single analytical reaction in which the two compounds differ sufficiently to be

readily distinguishable and this reaction demands the dry salt free from acid and in a fairly pure state; nor is it easy, even by the microscope to distinguish the presence of the tetrachloride in the mixture.

Ruthenium tetrachloride,  $\text{Ru}^{\text{IV}} \text{Cl}_4$  is easily reduced by stannous chloride to ruthenium trichloride,  $\text{Ru}^{\text{III}} \text{Cl}_3$  as follows:



In this the ruthenium reduction does not always stop at  $\text{Ru}^{\text{III}}$  but it sometimes reduced to  $\text{Ru}^{\text{II}}$  which gives the azure-blue solution which has already been touched on.

A stannous chloride solution of about  $\frac{\text{N}}{100}$  was used as a reducing agent. It was first standardized against .01064 N iodine solution. To prevent oxidation of the stannous chloride and changes in its normality a large burette was used for eight or ten titrations could be carried on successively with the same solution. A new solution of stannous chloride was made up every day.

Titrating the stannous chloride first with iodine using starch as an indicator it was found that the amount of stannous chloride used varied due to oxidation as follows:

I	cc. $\text{SnCl}_2$	Ratio of I to $\text{SnCl}_2$
1. 10cc	15.18	1:1.518
2. 10cc	15.20	1:1.520
3. 10cc	15.22	1:1.522

The iodine was then titrated with stannous chloride in an atmosphere of carbon dioxide. The stannous chloride reservoir and burette were kept in this atmosphere but still the results varied greatly as follows:

	ccI	ccSnCl <sub>2</sub>	Ratio of I to SnCl <sub>2</sub>
1.	10	10.48	1:1.048
2.	10	10.43	1:1.043
3.	10	10.50	1:1.050
4.	10	10.50	1:1.050
5.	10	10.49	1:1.049
6.	10	10.44	1:1.044

The flasks containing the iodine were also kept in an atmosphere of carbon dioxide, but the results still varied.

	ccI	ccSnCl <sub>2</sub>	Ratio of I to SnCl <sub>2</sub>
1.	10	10.34	1:1.034
2.	10	10.20	1:1.020
3.	10	10.24	1:1.024
4.	10	10.30	1:1.030
5.	10	10.33	1:1.033

These proceedings were repeated using hydrogen instead of carbon dioxide. When the reservoir and burette were kept in this atmosphere the results were as follows:

	ccI	ccSnCl <sub>2</sub>	Ratio of I to SnCl <sub>2</sub>
1.	10	10.52	1:1.052
2.	10	10.52	1:1.052
3.	10	10.54	1:1.054
4.	10	10.64	1:1.064

These results were better so the flask was also kept in an atmosphere of hydrogen with the following results:

	ccI	ccsnCl <sub>2</sub>	Ratio of I to SnCl <sub>2</sub>
1.	10	10.48	1:1.048
2.	10	10.44	1:1.044
3.	10	10.48	1:1.048
4.	10	10.49	1:1.049

Using a time factor of five minutes apart keeping the flasks of iodine without an atmosphere of hydrogen had a queer effect as follows:

I	SnCl <sub>2</sub>	Ratio of I to SnCl <sub>2</sub>
5 Minutes 10	11.20	1:1.120
10 Minutes 10	10.70	1:1.074
15 Minutes 10	10.70	1:1.070
20 Minutes 10	10.65	1:1.065
25 Minutes 10	10.58	1:1.058

If the flasks are kept in an atmosphere of hydrogen the titrations by the time factor show better results.

I	SnCl <sub>2</sub>	Ratio of I to SnCl <sub>2</sub>
5 Minutes 10	10.67	1:1.067
10 Minutes 10	10.92	1:1.092
15 Minutes 10	10.78	1:1.078
20 Minutes 10	10.80	1:1.080
25 Minutes 10	10.80	1:1.080

The first two were probably due to faulty manipulations or burette readings.

A ruthenium solution was then prepared by dissolving 0.034 grams of Rb<sub>2</sub> Ru<sup>IV</sup>Cl<sub>5</sub> OH, molecular weight 467, in 72.8 ml. of solution making it exactly N/100. It was kept strongly acidic with hydrochloric<sup>acid</sup> to prevent hydrolysis.

First the stannous chloride was titrated against iodine, then ruthenium, and again, iodine so that its normality would be known throughout the titration and any variation in normality by oxidation of the stannous chloride could be noted. A trial solution was first titrated and overstepped so as to observe the endpoint.

The following results were observed:

	SnCl <sub>2</sub>
10 cc I	10.38
10 cc I	10.30
10 cc Ru	41.20

The ruthenium solution turned a beautiful blue of the dichloride (?) on standing a short<sup>d</sup> while. This on further standing about five days turned back to the light yellow trichloride.

The ruthenium end-point is very difficult to observe and it must be carried on over a white plate and be carefully watched as each drop of stannous chloride strikes the tetrachloride. The dark brown of the tetrachloride is turned to a yellow at the point at which the drop strikes and when these drops of stannous chloride cause no further color change the end-point is reached. It is also best to carry a test solution carried just beyond the end-point for comparison.

In all the following titrations the reservoir of stannous chloride, the burette, and the flasks of solutions to be titrated were kept in an atmosphere of hydrogen.

The burette was refilled and iodine and ruthenium titrated again with the following results:



	SnCl <sub>2</sub>
10 cc I	10.81
10 cc I	10.78
10 cc Ru	10.78
10 cc Ru	10.78
10 cc I	10.78

Burette refilled		SnCl <sub>2</sub>
10 cc I		10.80
10 cc I		10.80
10 cc Ru		10.79
10 cc Ru		11.88 - overstepped
10 cc I		10.81

A new solution of N/100 ruthenium was prepared by weighing out 1.3232 grams of  $Rb_2 Ru^{IV}Cl_5OH$  and dissolving in  $1.3232 / .00467 = 283.3$  cc of solution also keeping it very acidic with hydrochloric acid to prevent hydrolysis.

In titrating the results were as follows:

A.	SnCl <sub>2</sub>
10 cc I	9.74
10 cc I	9.80
10 cc Ru	11.38 Overstepped to use as a test solution.
10 cc Ru	11.23
10 cc I	9.74

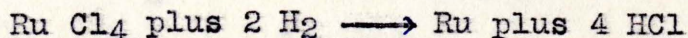
B. Burette refilled	SnCl <sub>2</sub>	C. Burette refilled	SnCl <sub>2</sub>
10 cc I	9.42	10 cc I	9.62
10 cc I	9.40	10 cc I	9.60
10 cc I	9.41	10 cc Ru	11.00
10 cc Ru	10.90	10 cc Ru	11.00
10 cc Ru	10.91	10 cc I	9.60
10 cc I	9.41		

D.	Burette refilled		Normality of Ru solution by titration
	10 cc I	9.58	A. .00971
	10 cc I	9.58	B. .01037
	10 cc Ru	11.00	C. .01006
	10 cc Ru	11.04	D. .01001
		Average	.01004 known checks very well with normality

The last 10 cc of ruthenium was taken from the bottle of solution and not allowed to stand in an atmosphere of hydrogen. For its end-point it turned a dirty green instead of yellow which is due to it being a mixture of the yellow trichloride and the blue dichloride (?). On standing it was all converted to the dichloride (?) giving an azure blue color. On heating slightly this turned a salmon pink due to the formation of the "aquo" salt  $Rb_2Ru(H_2O)Cl_5$ .

A solution of ruthenium tetrachloride was prepared by dissolving ruthenium residues in sodium hypochlorite and keeping it very strongly alkaline with sodium hydroxide. The solution was heated and chlorine passed through and as ruthenium tetroxide was formed it vaporized and was caught in cold 6 N hydrochloric acid which converted it into ruthenium tetrachloride. It was then concentrated by heating.

Two 5 cc samples of this tetrachloride were evaporated in weighed glass boats and put in a combustion tube. These were then heated strongly and hydrogen passed over them. The tetrachloride was reduced to pure ruthenium and the chlorine given off as HCl.



The boats were then reweighed as follows:

A. Boat plus ruthenium =	4.3508 grams
Boat =	4.3234 grams
Weight of ruthenium =	<u>.0274 grams</u>
B. Boat plus ruthenium =	4.1083 grams
Boat =	4.0805 grams
Weight of ruthenium =	<u>.0278 grams</u>

Average of the two samples = .0276 grams of ruthenium for 5 cc of solution.

1 cc of solution = ~~50~~ 5.52 mg. Ru.

A small amount of ruthenium was lost by spattering when evaporating the solution so a check analysis was run as follows being very careful that none was lost.

A. Boat plus ruthenium =	4.3515 grams
Boat =	4.3234 grams
Weight of ruthenium =	4.1088 grams
Boat =	4.0805 grams
Weight of ruthenium =	<u>.0283 grams</u>

Average of the two samples = .0282 grams of ruthenium for 5 cc of solution.

1 cc of solution = 5.64 mg. Ru.

The ruthenium solution just prepared was then titrated with stannous chloride with the following results.

	SnCl <sub>2</sub>	Burette refilled	SnCl <sub>2</sub>
10 cc I	9.70	10 cc I	9.68
10 cc I	9.68	10 cc I	9.68
10 cc I	9.68	5 cc Ru	7.12
5 cc Ru	7.10	5 cc Ru	7.10
5 cc Ru	7.11	5 cc Ru	7.12
5 cc Ru	7.10	5 cc Ru	7.12
10 cc I	9.68		

The average amount of stannous chloride used against 5 cc of ruthenium was 7.11 cc.

Ratio of I cc. of I to SnCl<sub>2</sub> = 1: .968

Normality of I = .01064N

$$\frac{.01064}{.968} = .01099 \text{ N} = \text{Normality of SnCl}_2$$

Ratio of 1 cc of SnCl<sub>2</sub> to Ru = 1: 1.422

$$\frac{.01099}{1.422} = .00773 \text{ N} = \text{Normality of Ru solution}$$

A normal solution of Ru contains 101.7 gms. per liter of solution.

Therefore the Ru solution contains:

$$\frac{101.7 \times .00773}{1000} = .00786 \text{ gms per cc} = 7.86 \text{ mg. per cc of solution.}$$

Results of reduction with hydrogen

1 cc of solution = 5.64 mg. Ru.

Results by titration

1 cc of solution = 7.86 mg. Ru.

The difference in these results were checked several times but the difference always persisted. This difference could be possibly due to the overstepping of the endpoint in titration due to the inability to get a sharp endpoint. But

in titrating the standard solution of  $Rb_2 Ru Cl_5 OH$  with stannous chloride the results checked very accurately so I conclude that some other factor must come in in titrating  $Ru Cl_4$  with stannous chloride tho I cannot find any reason for this.

Summary:

With known solution of N/100 the normality of  $Rb_2 Ru Cl_5 OH$  solution was checked by titrating with stannous chlorids as being .01004N. These checked very well.

In using  $RuCl_4$  the result by reduction with hydrogen *was i.e. of Ru solution contains 5.64mg Ru against*  
~~was~~ 1 cc. of Ru solution containing 7.86 mg. Ru by titration with stannous chloride standardized against iodine solution.