α - AND β -RUTHENIUM TRICHLORIDE

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SUMMARY

Published information on ruthenium trichloride is discrepant and confusing. Although two forms of the compound have been recognised, the means of preparing each in a pure form and of rigorously establishing its purity have been lacking. A detailed physico-chemical examination of the materials produced during a systematic re-investigation of the chlorination of ruthenium metal has led to the development of methods for the preparation of pure α - and β -RuCl₃. The properties of the two forms and their relation to each other are described.

INTRODUCTION

The products obtained by previous investigators of the reaction of chlorine or of mixtures of chlorine and carbon monoxide with metallic ruthenium have differed both in composition and properties. The results have been variously interpreted as indicating the production of the dichloride, the trichloride and the gaseous tetrachloride. We find that when the reaction is carried out under conditions in which the metal is in contact with a hot silicious surface, all the ruthenium chlorides listed in Table I together with ruthenium dioxide may be produced. The oxygen in the dioxide

TABLE I

α-RuCl₃	Black lustrous plates, insoluble; volatile above 600°C.
β-RuCl ₃	Dark brown, matt, fluffy, hygroscopic; soluble in aqueous alcohol.
Oxide chlorides	Hygroscopic, soluble; volatile above 300° C with decomposition.

and oxide chlorides is derived from the silica or silicate. As a result of a systematic study of the conditions of the reaction, we have been able to prepare the α and β forms of anhydrous ruthenium trichloride in a state of reasonable purity, and to study their properties.

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α - and β -ruthenium trichloride

JOLY¹ showed that finely divided ruthenium slowly increased in weight when heated at 360°C in chlorine, and that although conversion to chloride was never complete, a soluble form of RuCl₃ was produced. He also observed that carbon monoxide both increased the rate of reaction with chlorine at this temperature and allowed it to go to completion. Wöhler AND BALZ³ as well as REMY³ disproved an early suggestion that ruthenium dichloride was formed.

KOLBIN AND RYABOV⁴ examined the residues remaining when ruthenium was attacked by chlorine alone at temperatures from 280 to 840°C. They obtained (i) α -RuCl₃ in the form of brilliant black plates, insoluble in water and other solvents; (ii) a friable brown powder (which we term β -RuCl₃); and (iii) a dark brown hygroscopic material which corresponds to our oxide chlorides. HILL AND BEAMISH⁵, using the reaction between the metal and chlorine at 700°C, had previously recognised the first and third of these constituents and obtained a distinctive X-ray pattern for each. In the course of their work, KOLBIN AND RYABOV⁴ studied the transformation from the β to the α form and found that it was irreversible.

Our earlier preparative work with chlorine, or with mixtures of chlorine and carbon monoxide, gave products which varied both in properties and composition. The criteria we then used in identifying the materials included appearance, solubility, infra red spectra and X-ray diffraction patterns. These enabled us to show that the carbonyl compounds produced by mixtures of chlorine and carbon monoxide persist at temperatures up to 300°, that unconverted metal frequently remained, and that ruthenium dioxide could be formed.

The indexing of the X-ray diffraction lines of a compound (subsequently recognised as β -RuCl₃) that was present in preparations at relatively low temperatures aided progress, but the limitations of X-ray diffraction in providing quantitative information prevented our knowing whether or not a given specimen consisted of pure α or β ruthenium trichloride or was contamined up to 5% of the other form.

Further advance came with the application of visible and u.v. absorption spectra and the measurement of magnetic susceptibility. Evidence from the first, along with the knowledge of the properties of ruthenium aquochloro complexes developed in these laboratories⁶, enabled the oxide chlorides present in the products to be recognised; the second⁷, by showing that the x and β forms of ruthenium trichloride differed markedly in magnetic properties, provided a sensitive criterion for recognising when these forms were pure.

Although WÖHLER AND BALZ² found no evidence to support the existence of the tetrachloride, it has recently been claimed^{8,9} that this is formed when ruthenium trichloride is heated in a stream of chlorine at temperatures of about 750°C. We have frequently noticed the deposition of coloured volatile products during the preparation or manipulation of our materials at temperatures above 300°C. When formed below 600°C these have had the properties (solubility, adsorption spectra) of the oxide chlorides that are produced by heating the mixture of Ru(IV) compounds known as commercial "ruthenium trichloride". The presence of these oxide chlorides might, at least in part, account for some of the observations on which the formation of ruthenium tetrachloride has been postulated.

RESULTS

β -RuCl₃

Preparation

The earlier preparations (Table II, Serials 1-4) made by heating ruthenium metal in a stream of CO/Cl₂ (1:3 volume) at 360-390°C for 4-8 h, were usually found to confirm closely to the composition required for RuCl₃, but there was often some (1-3%) unconverted metal. The X-ray patterns showed weak lines for α -RuCl₃ but the magnetic susceptibilities of the materials, though much lower than those of the α -form, varied widely (Table II) suggesting the presence of different amounts of α -RuCl₃ in the various preparations.

TABLE II

PREPARATIONS OF β -RuCl₃

Serial	Ru	Temp.	Time	Analysis (%)		Ru*	10 ⁶ × XM	a-RuCl ₃ in
No.	metal used (g)	(°C)	(h)	Ru	Cl	metal	at 20°K (e.m.u.)	products (from χ _M) (%)
r	4	380	8	49.0	49.0	т	7,600	23
2	3.4	360	5	48.3	49.5	т	2,500**	30
3	0.6	360	10	48.8	50.0	N.D.	770	2.5
4	1.0	360	36	49.0	49.9	Т	1,590	5
5	0.5	340	15	48.3	50.5	N.D.	220	1.0
6	0.5***	330	5	49.4	48.2	Т	130**	2.5
7	2.4	340	20	•- •	•	~10%	-	∼5* [°]
		Calculated	for RuCl	3: 48.7	51.3			

* Identified by X-ray diffraction; T = Trace; N.D. = Not Detected.

** Measurements made at 77°K.

*** One of 8 similar batches.

Note: For the calculation, χ'_M was obtained by adding a diamagnetic correction of 100×10^6 units to χ_M , and it was assumed that χ'_M for β -RuCl₃ is ~ 0 and $\chi'_M \cdot T$ for α -RuCl₃ in this environment is 0.65 at the temperatures used.

Contamination by α -RuCl₃, due partly to local overheating, was reduced by using (i) small amounts (0.5 g) of metal sponge spread evenly over the Vycor tube, and (ii) lower temperatures (330–340°C). The unconverted metal remaining in the chloride was reduced to less than 1% (Table II, Serial 5) by lightly grinding the product, after treatment for 4–6 h, and reheating it in CO/Cl₂ at 330–340°C for a further period. It was found to be advantageous to bring the material up to the required temperature, and subsequently to cool it, in chlorine alone. It was eventually found that the magnetic susceptibility of α -RuCl₃ below 100°K is sufficiently large to allow even 1% of the α form in the β form to be detected (Table II).

Formation

 β -RuCl₃, usually contaminated with oxygen-containing compounds, can be produced at relatively low temperatures from certain Ru(III) compounds. Thus KRAUSS¹² showed that it was formed by the reaction of hydrogen chloride with ruthenium(III) hydroxide.

We find it to be the main constituent in the product from the following sequence of reactions:

Ru(IV) chloro complexes in EtOH (with 0.6 M H₂O) $\xrightarrow{\text{reflux, }\frac{1}{2}h}$ Ru(III) $\xrightarrow{\text{evaporate}}$ Black residue

An X-ray examination of the residue showed the presence of β -RuCl₃ and chemical analyses that it had the atomic ratio Ru/Cl I : 2.6. The average oxidation state of the ruthenium in the product was + 3.77.

Properties

 β -RuCl₃ was produced as a fluffy, dark-brown powder with a low tap-density and high surface-area. Moisture absorbed from the air could be removed under vacuum at room temperature. When heated without being so dried, not all the water was lost, some reacting with the chloride to form oxygenated products. These were detected (i) by the oxygen content (I-2%) and the presence of X-ray lines for RuO₂, and (ii) by D.T.A. which showed that an exothermic reaction occurred at *ca.* 350°C; this reaction did not take place with a dried sample.

 β -RuCl₃ is monotropic. We find that the conversion $\beta \rightarrow \alpha$ occurs at rather lower temperatures than that which had been previously reported⁴ (*i.e.* 500° C). Differential thermal analysis at a heating rate of 10°/min showed a slow and weak exothermic reaction ($\Delta H < 3$ kcal) over the range 450-510°C. Using the X-ray diffraction lines as a means of analysis, we were unable to detect any conversion to α-RuCl₃ after it had been heated in a sealed capillary at 445°C for I day, but the lines of α -RuCl₃ appeared after 1 day at 461 + 3°C, conversion being virtually complete after 4 days. In another set of experiments, β -RuCl₃ was heated in static argon for periods of 4–12 h at successive 10° intervals between 400 and 450°C and the degree of conversion followed by the changes in the magnetic susceptibility; the presence of α -RuCl₃ was detected at 440 + 5°C. Similar experiments with less pure samples of β -RuCl₃ gave results which suggested that the impurities enable the transition to occur to a certain extent at about 50°C below the temperature for pure β -RuCl₃. One impure preparation (Table II, Serial 4) even showed a small increase in susceptibility, (e.g. from 1590×10^{-6} to 1920×10^{-6} e.m.u. at 20° K) after being heated for 16 days at a temperature as low as 350°C.

Although β ruthenium trichloride coloured a number of non-polar solvents, dissolution was slight and, since the solubility increased when moisture was present, it was largely ascribed to traces of oxygenated products. A solvent in which the solubility was sufficient for a cryoscopic measurement to be made was not found.

The reflectance spectrum of β -RuCl₃ was relatively featureless from 350-800 m μ , with however the suggestion of a broad peak at *ca*. 400 m μ . In contrast, α -RuCl₃ gave a constant absorption over the whole range examined.

α -RuCl₃

Preparation

Although this form is produced in the reaction between metal and chlorine at 600–700°C, the product is contaminated by oxide chloride and by ruthenium dioxide when the metal is in contact with silica. Presumably the impurities arise through the successive reactions:

 $\begin{array}{ll} \mathrm{Ru} + \mathrm{SiO}_2 + \mathrm{Cl}_2 \rightarrow \mathrm{Ru}_2\mathrm{OCl}_6 + \mathrm{SiCl}_4 \text{ ,} \\ \mathrm{Ru}_2\mathrm{OCl}_6 & \rightarrow \mathrm{RuO}_2 + \mathrm{RuCl}_3 \text{ .} \end{array}$

The use of chlorine purified by fractional distillation and the complete exclusion of atmospheric oxygen during chlorination made it clear that the silica was the source of the oxygen. This conclusion is supported by the smaller amount of oxygen in the products when a porcelain or Vycor glass tube was substituted for silica. A long series of chlorinations of ruthenium metal, in the form of either sponge as supplied by Johnson Matthey Ltd., or reactive metal prepared by the reduction *in situ* of commercial ruthenium trichloride at 700–750°C with hydrogen, failed to give α -RuCl₃ uncontaminated by ruthenium dioxide and oxide chloride. The results for a typical run are given in Table III (Serial No. 1).

TABLE III

PREPARATIONS OF α -RuCl₃

Serial No.	Mode of preparation	Temp. (°C)	Time (h)	Analysis (%)		X-ray	
				\overline{Ru}	Cl	examination*	
						Ru	RuO_2
I	Ru in Cl2	640	3	47.0	46.0	Т	Т
2	Ru in CO $+$ Cl ₂ direct	600	15	49.0	50.8	N.D.	N.D.
3	β -RuCl ₃ in chlorine	650	2	48.7	50.5	N.D.	N.D.
4	β -RuCl ₃ in argon	450	8	**	**	N.D.	N.D.
5	β -RuCl ₃ in chlorine	550-600	2	48.6	50.4	N.D.	N.D.
6	eta -RuCl $_3$ in argon	550	8	49.6	48.6	~ 5%	N.D.

* N.D. = Not Detected; T = Trace.

** From the β -RuCl₃ listed in Table II, Serial 5.

Notes: (i) The amount of ruthenium used in the preparations varied from 0.25 to 3 g.

(ii) Mixtures of CO/Cl_2 in the ratio of I:3 by volume were used.

(iii) In Serial 2, oxide chlorides (ca. 2%) were removed from the product by an ethanol wash after a heating time of 12 h; the final heating for 3 h was carried out in chlorine. For Serial 5, a similar ethanol wash removed no ruthenium.

Satisfactory preparations were made in siliceous containers by either of the following methods (i) by the procedure of REMY³, *i.e.* by heating the metal at appropriate temperatures in a mixture of the two gases (Table III, Serial No. 2); or (ii) by first producing β -RuCl₃ by this means and subsequently converting it to α -RuCl₃ by heating in chlorine or argon (Table III, Serials Nos. 3–5): with argon, the temperature must not be allowed to exceed *ca.* 500°C owing to the tendency for ruthenium metal to be formed (Table III, Serial No. 6), as is to be expected from the dissociation pressure¹³.

The magnetic susceptibilities (Table IV, Serial Nos. 1–3) of specimens of α -RuCl₃ produced in each of these ways were substantially higher than the contaminated products made by heating ruthenium in chlorine alone (Serial No. 5): moreover they were higher than the values (Table IV) reported by earlier workers, presumably due to impurities in their preparations. It appears that at least one of these earlier preparations was made by heating commercial ruthenium trichloride in a stream of chlorine; this procedure we have found gives a mixture of α -RuCl₃ and the dioxide after 3 h at 680°C.

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TABLE IV

Serial No.	Preparation	Starting	10 ⁶ × XM	Ітри-	
		material	At 77°K	At 292–298°K	rity* (%)
I	Table III, Serial 3	β-RuCl ₃	8,150	2,130 (294°)	
2	Table III, Serial 4	β-RuCl ₃	8,200	2,080 (293°)	
3	Table III, Serial 5	β-RuCl ₃	8,450	2,130 (292°)	
4	CABRERA AND FAHLENBRACH ¹²	?		1,990 (292°)	5
5	Table III, Serial 1	Ru & Cl ₂		1,900 (293°)	10
6	EPSTEIN AND ELLIOTT ¹³	"Trichloride" and Cl ₂	7,140	1,710 (296°)	18
7	GUTHRIE AND BOURLAND ¹⁴	?		1,495 (298°)	30

MAGNETIC SUSCEPTIBILITY OF PREPARATIONS OF X-RuCl₃

* Calc. on the assumption that $10^6 \times \chi_M$ is 2,130 e.m.u. at 293°K for α -RuCl₃ and negligible for the impurities.

Ruthenium carbonyl chloride

This was observed as a yellow compound when ruthenium metal was heated in CO/Cl₂ mixtures at temperatures between 250° and 310°C. At 310°, it appeared as a sublimate (Found: Ru, 43.6; Cl, 30.2%: Ru(CO)₂Cl₂ requires: Ru, 44.4; Cl, 31.0%). It had strong infra-red bands at 2083 and 2024 cm⁻¹ and dissolved in hot water to give a yellow solution with $\lambda_{max} = 365 \text{ m}\mu$, $\varepsilon_{Ru} = 228$.

EXPERIMENTAL

Analysis

Ruthenium was usually determined as the metal by reduction of the chloride by hydrogen in a silica boat at 600–800°C until the weight was constant. Chlorine was determined by Volhard's method after fusion with sodium peroxide at 500°C for 30 min in a platinum dish, followed by dissolution in water, precipitation (with acetone) and removal of the ruthenium as the dioxide. Dissolution of this dioxide in alkali followed by estimation of the ruthenium spectrophotometrically by WOODHEAD's method¹⁰ was also used as a method.

Oxygen was determined as carbon dioxide after fusion in a carbon crucible in a stream of inert gas¹¹.

Magnetic susceptibilities

The specimens used were dried *in vacuo* at room temperature immediately prior to use. Some determinations between room and liquid nitrogen temperatures were made by the Gouy method. At lower temperatures and to obtain several values over a range of temperatures, the Faraday method was used with 10–20 mg samples.

X-ray examination

For the X-ray powder photographs taken at room temperature a Guinier focussing camera was employed; for those taken at higher temperatures the specimens were mounted in platinum-coated silica capillaries, and the patterns were recorded by means of a Unicam S-150 camera. The actual temperatures of the measurements were deduced from the lattice parameter of the platinum.

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Note added in Proof (May 6th, 1965)

 α -RuCl₃ of high purity has also been prepared as a sublimate by a modification of the procedure of that for Serial No. 5, Table III. 2 g of β -RuCl₃, made in a τ in. diameter Vycor tube at 380°C, were converted to α -RuCl₃ in a stream of chlorine by raising the temperature to 650°C: traces of violet oxide chlorides were volatilised at this temperature. The α -RuCl₃ was then completely sublimed in chlorine at 730°C over a period of hours and deposited in the tube separately from the violet chlorides.

The value of χ_M determined by the Faraday method on a large (50 mg) sample of the product, kept free from moisture, was 2310 × 10⁻⁶ e.m.u. at 289°K. As a similar value, 2316 × 10⁻⁶ e.m.u. at 293°K, has also been found by the same susceptibility procedure on a well-dried sample of the α -RuCl₃ reported as Serial 3 in Table IV, it is concluded that 10⁶ × χ_M for α -RuCl₃ at 293°C is about 2300 e.m.u., rather than 2130 e.m.u. as assumed in Table IV.

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