CCCVIII.—*Rhenium Tetrachloride and the Rhenichlorides.*

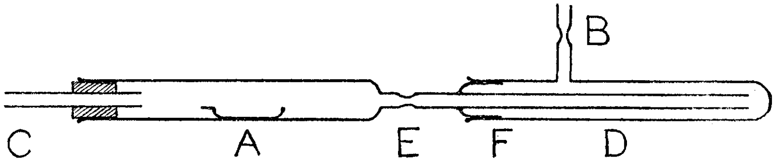
By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON, and ERIC MAURICE STODDART.

THE chlorides of rhenium have been previously investigated by Noddack (*Z. Elektrochem.*, 1928, **34**, 627; *Z. angew. Chem.*, 1931, **44**, 215), who describes two compounds, thus: " Durch Einwirkung von Chlorgas auf Rheniumpulver einsteht bei gelindem Erwarmen ein tiefgrünes, leicht flüchtiges Chlorid von der Formel $ReCl_7$ das bei gewöhnlicher Temperatur grüne Kristalle bildet. . . . Bei Erhitzen von Rheniummetall mit Chlorgas auf 500° oder bei der thermischen Zersetzung von $ReCl_7$ entsteht ein braunes ebenfalls flüchtiges Chlorid das angenähert die Zusammensetzung $ReCl_6$ ergab. . . ."

We have been unable to prepare either of these substances but have found that the combination of rhenium and chlorine under the conditions described by Noddack yields, as the main product, a black compound, hitherto unobserved, which proved to be *rhenium tetrachloride*, $ReCl_4$. This new chloride resembles osmium tetrachloride especially in yielding *rhenichlorides* (M_2ReCl_6) analogous to the osmichlorides (M_2OsCl_6). No trace of Noddack's green compound has been observed, but the black tetrachloride was invariably accompanied by traces of a brown, well-crystallised substance, melting sharply at about 21°, and decomposed by water to yield a dark colloidal solution. Unfortunately, this substance has, so far, been obtained only in quantities totally insufficient for analysis.

Noddack (*loc. cit.*) observed that when metallic rhenium was heated in bromine and in iodine, black volatile halides, readily hydrolysed to hydrogen halide by atmospheric moisture, were produced. To these no formulæ were ascribed, since the traces obtained were inadequate for such characterisation. The present authors have confirmed these observations, and, by analogy with the chlorine compound, suggest that these products are probably tetrahalides.

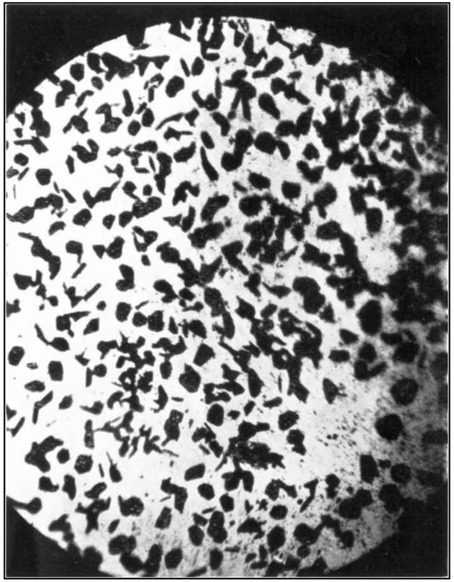
FIG. 1.



EXPERIMENTAL.

Rhenium Tetrachloride.—A porcelain boat containing metallic rhenium was placed in A (Fig. 1) and the whole apparatus, which was constructed in Pyrex glass, was evacuated at B by means of a "Hyvac" pump. Chlorine, dried by passage over phosphoric oxide, was slowly admitted at C, and when it gave a pressure slightly exceeding the atmospheric, B was opened to the air. When the metal was heated to about 250° in the atmosphere of pure chlorine thus obtained, a sublimate of glistening black needles settled in D. For the purpose of analysis, D, after being sealed off at E, was evacuated for 15 minutes through B, and was finally filled with dry air and sealed off at that point. After D and its contents had been weighed, the tube was opened at the ground joint, F, and the product completely washed into a beaker with water. By subsequently drying and weighing the two separate parts of D, the weight of chloride could be ascertained.

Plate Ia.

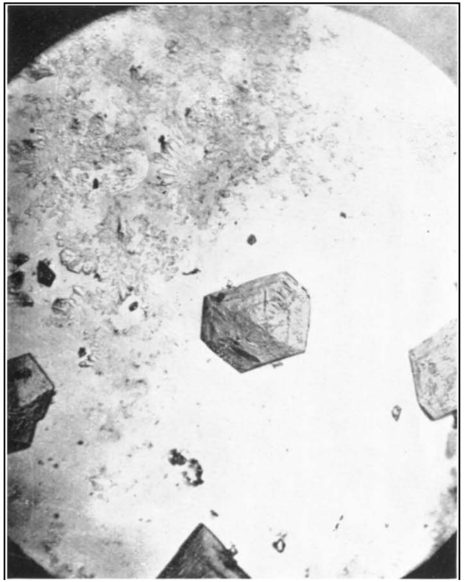


Magnification × **140.**

Plate Ib.

Magnification × 80.

Plate Ic.



Magnification × 80.

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The rhenium in the material was estimated by oxidising it to per-rhenic acid and subsequently reducing this to the dioxide. Incidentally, it was found that oxidation by nitric acid was unsuitable through loss of the volatile heptoxide during subsequent evaporation, and in consequence oxidation was effected by ammoniacal hydrogen peroxide. This proved entirely satisfactory. The solution was boiled to remove excess of the reagents and to reduce the bulk to 25 c.c., and then, after acidification with hydrochloric acid, the per-rhenate was reduced with metallic zinc in the manner already described (Briscoe, Robinson, and Stoddart, this vol., p. 666). The rhenium was weighed as $ReO_2,2H_2O$.

The chlorine was estimated by oxidation of the material from the weighing vessel with nitric acid and subsequent precipitation as silver chloride in the ordinary way.

The results given in Table I clearly establish the compound formed as *rhenium tetrachloride*. This has the appearance indicated by Plate IA and may be sublimed in either air or chlorine; it combines with alkali chlorides, forming rhenichlorides, and is decomposed by ammonia gas and by water.

TABLE I.

Expt.	Chloride, g.	$ReO_2,2H_2O$, g.	Re, %.	Chloride, g.	AgCl, g.	Cl, %.
1	0·1059	0·0820	56·72	0·1726	0·3035	43·50
2	0·1567	0·1214	56·75	0·1187	0·2027	42·25
3	0·1302	0·1018	57·27	0·1527	0·2686	43·52
4	0·1117	0·0860	56·40	0·1326	0·2301	42·92
		Mean	56·79		Mean	43·05
		$ReCl_4$ requires	56·75		$ReCl_4$ requires	43·19

No evidence of the formation of a lower chloride was obtained when rhenium was heated in dry hydrogen chloride at temperatures up to 900°, the metal being unattacked under these conditions.

The Alleged Green and Brown Chlorides.—In chlorinating the metal we invariably obtained at the beginning of each operation a trace of material which crystallised as very fine needles up to 0·5 cm. in length (Plate IB), brownish by reflected and dichromate-red by transmitted light, which melted sharply to a dark brown liquid at 21°. This material could be distilled from one part of the tube to another in an atmosphere of chlorine, the liquid resolidifying at about 5°, but when heated in air or a vacuum, it dissociated, leaving a dark stain on the glass. On hydrolysis in a stream of moist air, the material first rapidly turned black and then, as the passage of air continued, became steel-grey, after which it deliquesced and changed through dark blue and blue-green, becoming eventually bright green. The green colour appeared to be due to the presence of both blue and yellow material. The addition of water to the substance at any stage produced a dark colloidal solution.

The formation of this brown, low-melting material took place only for a few seconds after reaction between the metal and chlorine began, and then tetrachloride was produced in its place. This led to the idea that the brown crystals resulted either from metallic impurity or from the presence of oxygen. Comparative experiments with such possible contaminating metals as molybdenum, tungsten, and osmium ruled out the first possibility, whilst the fact that the addition of various proportions of oxygen to the chlorine did not increase the yield, cast a doubt on the second. Some other experiments whereby we sought to elucidate the matter together with their results are here given : (i) Heating the metal in hydrogen and immediately substituting chlorine for hydrogen : yield unaffected. (ii) Chlorinating the di- and the hept-oxide with carbon tetrachloride : yield, a trace only. (iii) Chlorinating metal with undried chlorine : yield, nil. (iv) Chlorinating a mixture of dioxide and metallic rhenium : yield unaffected. (v) Chlorinating metal from a fresh supply : yield unaffected. (vi) Chlorinating the disulphide and the heptasulphide : yield unaffected, but a white substance was also observed which, when allowed to hydrolyse slowly in air, gave a purple liquid.

The Rhenichlorides.—It is known that a mixture of osmium and potassium chloride when heated in chlorine yields potassium osmichloride (K_2OsCl_6). Potassium rhenichloride has been similarly obtained and from it a number of other rhenichlorides have been prepared.

A mixture of metallic rhenium and potassium chloride, ground together in the proportions required for K_2ReCl_6, was spread along a Pyrex tube, and after all the air had been removed by a stream of chlorine, the tube was heated until the powder melted to yellowish-brown globules. This product was finely powdered, and the soluble portion extracted from the unattacked metal as a green aqueous solution which, when concentrated in a desiccator, yielded green crystals up to 0·5 cm. diameter (Plate Ic) together with some potassium chloride. On no account, however, must the solution be warmed, since at about 25°, decomposition sets in with the formation of a dark colloidal solution (compare the osmichlorides). The green crystals were hand-picked and well dried, and proved to be *potassium rhenichloride* (see below), which is stable in air and is not dissociated when heated to 300°.

We have also synthesised this compound by slowly volatilising rhenium tetrachloride over heated potassium chloride.

Silver rhenichloride, by means of which the composition of the potassium salt was established, was obtained quantitatively therefrom by adding excess of silver nitrate to an aqueous solution of a known weight of potassium rhenichloride. The precipitated silver rhenichloride (see below) was collected on a fritted-glass crucible, washed, dried over phosphoric oxide, and weighed. The salt is orange in colour, insoluble in water, and not obviously crystalline: it decomposes on strong heating, giving traces of black rhenium tetrachloride. It is evidently formed when a solution of rhenium dioxide in the minimum quantity of hydrochloric acid is treated with aqueous silver nitrate, for the precipitate thus obtained is distinctly yellowish-orange. The ratio $Ag_2ReCl_6 : K_2ReCl_6$ found in the above conversion is that theoretically required (Table II).

TABLE II.

K_2ReCl_6, g.	Ag_2ReCl_6, g.	$Ag_2ReCl_6 : K_2ReCl_6$.
0·0913	0·1176	1·288
0·1067	0·1370	1·284
0·1024	0·1312	1·281
0·1127	0·1451	1·287
	Mean	1·285
	$Ag_2ReCl_6 : K_2ReCl_6$ requires	1·288

The chlorine in the rhenichloride was estimated by heating it in a silica sleeve-tube in a tube furnace through which passed a stream of hydrogen dried over phosphoric oxide. The gases leaving the furnace were passed into silver nitrate solution, and the resulting silver chloride was separated and weighed. The silver, on the other hand, was estimated by washing the sleeve-tube out with nitric acid and precipitating the metal as chloride. The use of a sleeve-tube which extended beyond the heated zone was essential, since traces of material tended to be removed by the gas stream during the reduction. The results (Table III) show that the substance was silver rhenichloride, and this was confirmed by a rough estimation of the percentage of rhenium by the dioxide method.

TABLE III.

Ag_2ReCl_6, g.	AgCl from HCl, g.	AgCl from Ag, g.	Cl, %.	Ag, %.
0·1057	0·1484	0·0492	34·74	35·04
0·1268	0·1779	0·0592	34·71	35·14
0·1026	0·1450	0·0480	34·97	35·22
0·0902	0·1249	0·0420	34·29	35·04
		Mean	34·68	35·11
		Ag_2ReCl_6 requires	34·60	35·10

The addition of an aqueous solution of potassium rhenichloride to solutions of various metallic salts showed that the following ions gave insoluble rhenichlorides: silver (orange), mercurous (deep yellow), thallous (canary-yellow). No precipitate of a rhenichloride was obtained with solutions containing the following ions : lead, cupric, barium, cobalt, nickel, manganese, magnesium, ferrous, ferric, zinc, lithium, and mercuric.

The behaviour of metallic rhenium when heated with bromine and with iodine confirmed the observation of Noddack (p. 2264). It is probable that a rhenibromide is formed when a mixture of metallic rhenium and potassium bromide is heated in bromine vapour. The reddish product is, however, less stable than the rhenichloride, being at once decomposed by cold water.

Summary.

No evidence has been obtained of the existence of the reported rhenium hexa- and hepta-chlorides. Rhenium tetrachloride, which has not been previously observed, is the primary product of heating the metal in chlorine. Potassium rhenichloride and other rhenichlorides have been prepared.

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UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.
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