226. New Fluorides and Oxyfluorides of Rhenium.

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The preparation of the pentafluoride, tetrafluoride, oxytetrafluoride, and oxytrifluoride of rhenium is described. The magnetic moments of the pentafluoride and oxytetrafluoride have been measured over the temperature range 90—300° K.

THERE is little information about the fluorides and oxyfluorides of rhenium. Ruff showed that rhenium forms a hexafluoride but not a heptafluoride—a conclusion which has since been amply confirmed. Ruff and his co-workers also reported that a green tetrafluoride is formed by the reduction of the hexafluoride with hydrogen or sulphur dioxide at high temperatures, and claimed[1] that rhenium forms four oxyfluorides; $ReOF_4$, ReO_2F_2, ReO_3F, and possibly $ReOF_2$. Later work has confirmed the trioxyfluoride,[2] but the formulæ of the sexivalent oxytetrafluoride and dioxydifluoride have been in doubt since

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[1] Ruff and Kwasnik, *Z. anorg. Chem.*, 1934, **219**, 65.

[2] Englebrecht and Grosse, *J. Amer. Chem. Soc.*, 1954, **76**, 2042.

the discovery[3] of the septavalent compounds $ReOF_5$ and ReO_2F_3, and there has been no confirmation of the tetrafluoride.

TABLE 1. *Reduction of rhenium hexafluoride by the carbonyls of molybdenum, tungsten, and rhenium.*

Reagents	Reaction products
ReF_6 (excess) + $Re_2(CO)_{10}$	$ReOF_4$ and residue
ReF_6 (large excess) and $W(CO)_6$	$ReOF_4$, WF_6, and impure ReF_4
ReF_6 (small excess) and $W(CO)_6$	$ReOF_4$, ReF_5, WF_6, and impure ReF_4
ReF_6 (small excess), WF_6 (large excess) and $W(CO)_6$	ReF_5 and impure ReF_4
ReF_6 + $Mo(CO)_6$	$ReOF_4$, ReF_5, MoF_5, and residue

The present work was begun with the object of preparing carbonylrhenium fluorides. Although unsuccessful in this, nonetheless the enquiry has resolved some of the problems outlined above.

Preliminary experiments showed that fluorine behaves towards decacarbonyldirhenium much as it does towards hexacarbonyltungsten. No perceptible reaction occurs at 25°; at higher temperatures rhenium hexafluoride and products of indefinite composition are formed. Indirect methods in which rhenium hexafluoride was reduced by carbonyls of molybdenum, tungsten, and rhenium were therefore tried.

These experiments (Table 1) have yielded directly rhenium oxytetrafluoride, which does not have the properties ascribed to it by Ruff, and the unknown rhenium pentafluoride. In addition, impure rhenium tetrafluoride is formed. From the oxytetrafluoride we have prepared the new quinquevalent rhenium oxytrifluoride. From the pentafluoride we have obtained the pure tetrafluoride, which is quite distinct from the material described by Ruff.

Rhenium Oxytetrafluoride.—Rhenium oxytetrafluoride is a blue crystalline solid which melts at 108° to a blue liquid. At 171° under atmospheric pressure the liquid boils to a colourless vapour. At 250° the vapour attacks "Pyrex" with the formation of the oxytrifluoride. With water the oxytetrafluoride behaves as does rhenium hexafluoride, giving per-rhenic acid, hydrated rhenium dioxide, and hydrofluoric acid. Rhenium oxytetrafluoride is very reactive; it attacks carbon tetrachloride with the formation of a red-brown solution ($ReCl_5$), and is quickly attacked by moist air.

The magnetic moment of the oxytetrafluoride (Table 3) is as expected for a rhenium(VI) compound; it is lower than the value calculated for one unpaired spin ($\mu = 1{\cdot}88$ B.M.) and varies with temperature as predicted by Kotani (cf. ref. 4).

Rhenium Oxytrifluoride.—"Pyrex" glass is attacked slowly at 250° by the oxytetrafluoride to give black, non-volatile rhenium oxytrifluoride. Since the formation of this compound should involve the concurrent appearance of a rhenium(VII) compound, we looked for the volatile oxyfluorides $ReOF_5$ and ReO_2F_3 but these escaped detection, probably because the quantities of material were so small.

The oxytrifluoride has a tetragonal unit cell ($a = 8{\cdot}54$ Å; $c = 8{\cdot}21$ Å). It is very hygroscopic and gives a blue aqueous solution which presumably contains a complex oxyfluoro-ion.

Rhenium Pentafluoride.—Rhenium pentafluoride is a green or yellow-green crystalline solid which melts at 48° to a viscous yellow-green oil. The liquid crystallises with difficulty on cooling. At its boiling point (240°) it disproportionates rapidly into hexafluoride and the tetrafluoride; this dismutation is evident in a vacuum at 180° and is apparently irreversible

$$2ReF_5 \longrightarrow ReF_6 + ReF_4$$

At lower temperatures the pentafluoride gives a colourless vapour and can be sublimed or distilled unchanged under a good vacuum.

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[3] Aynsley, Peacock, and Robinson, *J.*, 1950, 1622.

[4] Hargreaves and Peacock, *J.*, 1958, 3776.

Rhenium pentafluoride is noticeably less reactive than the oxytetrafluoride but attacks carbon tetrachloride at once. It is decomposed readily by moist air but can be handled in a dry box. It is attacked violently by water, yielding per-rhenic, fluororhenic, and hydrofluoric acid, and hydrated rhenium dioxide. Analysis of the products of hydrolysis shows that the three rhenium compounds are formed in nearly equal amounts in accordance with the equation:

$$3ReF_5 + 6H_2O \longrightarrow ReF_6^{2-} + ReO_4^- + ReO_2 + 9F^- + 12H^+$$

The magnetic behaviour of the pentafluoride (Table 3) is complicated; the large value of θ shows that there is antiferromagnetic interaction.

Rhenium Tetrafluoride.—The residue from the thermal decomposition of the pentafluoride is pale blue, powdery rhenium tetrafluoride. The salt, which sublimes at about 300° in a high vacuum, is hydrolysed immediately by water to rhenium dioxide and hydrofluoric acid (cf. molybdenum tetrafluoride[5]). It has not been possible to index the *X*-ray powder photograph.

DISCUSSION

The reduction of rhenium hexafluoride by carbonyls is clearly a complicated process, since in addition to the expected formation of lower fluorides the oxytetrafluoride appears. This can only mean that the liberated carbon monoxide is taking part in the reaction, and that oxygen is being abstracted from it by rhenium, presumably in exchange for fluorine. The formation of oxyfluoride is favoured by vigorous reaction conditions, and the formation of pentafluoride by milder conditions.

TABLE 2. *Physical properties of the transition-metal oxytetrafluorides.*

	M. p.	B. p.	Colour	Ref.
$MoOF_4$	97°	180°	White	*a*
WOF_4	110	185	White	*b*
$ReOF_4$	108	171	Blue	

a Ruff and Eisner, *Ber.*, 1907, **40**, 2931. *b* Ruff, Eisner, and Heller, *Z. anorg. Chem.*, 1907, **52**, 256.

Rhenium oxytetrafluoride, apart from its colour, resembles the analogous molybdenum and tungsten compounds closely in appearance, melting and boiling points (Table 2), and chemical behaviour. Like them it is also formed by slow decomposition of the hexafluoride in " Pyrex " and glassware, and hence must have been overlooked several times in the past.

Rhenium pentafluoride, as is evident from its preparation and thermal decomposition, is unstable or metastable. The disproportionation recalls that of vanadium tetrafluoride [6] but is otherwise unparalled among transition-metal fluorides. The viscosity of the liquid from visual observation is of the same order as that of antimony and molybdenum pentafluoride, and implies a considerable degree of association. The hydrolysis and the large antiferromagnetic contribution to the magnetic moment of the solid also suggest a polymeric structure. The properties ascribed by Ruff and Kwasnik to rhenium tetrafluoride are remarkably like those to be expected for a mixture of the tetrafluoride and pentafluoride. It is, of course, possible that they obtained another form of the tetrafluoride, but our own experience with these substances has shown how easily confusion may arise.

EXPERIMENTAL

Reagents.—Rhenium and tungsten hexafluorides were prepared from the elements. Carbonyls were resublimed in a vacuum.

Action of Rhenium Carbonyl on Rhenium Hexafluoride.—Rhenium carbonyl dissolved in liquid rhenium hexafluoride with the intermittent evolution of carbon monoxide; the solution, which was initially yellow, became blue-green, and blue crystals appeared on the sides of the

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[5] Peacock, *Proc. Chem. Soc.*, 1957, 59.

[6] Ruff and Lickfett, *Ber.*, 1911, **44**, 506.

vessel above the liquid. After the excess of rhenium hexafluoride had been pumped off a blue-green solid remained which, at 40° under a high vacuum, yielded crystals of *rhenium oxytetrafluoride*, which sublimed from the reaction bulb (Found: Re, 66·7; F, 28·1. ReOF$_4$ requires Re, 66·9; F, 27·3%). A brown residue of indefinite composition remained.

Action of Tungsten Carbonyl on Rhenium Hexafluoride.—(a) *Large excess of rhenium hexafluoride.* The tungsten carbonyl dissolved quietly in liquid rhenium hexafluoride with the steady evolution of carbon monoxide; the initially yellow solution changed to blue, and the products were rhenium oxytetrafluoride (Found: Re, 66·8; F, 28·0. Calc. for ReOF$_4$: Re, 66·9; F, 27·3%), tungsten hexafluoride, and a pale green or brown residue which contained tungsten (Found for a typical sample: Re, 68·3; F, 25·2. Calc. for ReF$_4$: Re, 71·0; F, 29·0%).

(b) *Small excess of rhenium hexafluoride.* The colour change stopped at grass-green. After the rhenium and tungsten hexafluoride had been pumped off there remained a green solid, m. p. 59° (decomp.), and blue crystals of rhenium oxytetrafluoride appeared. When the temperature was raised further a yellow-green oil distilled which at 25° gradually crystallised. This was *rhenium pentafluoride* (Found: Re, 66·5; F, 33·6. ReF$_5$ requires Re, 66·2; F, 33·8%). The residue was impure tetrafluoride (Found: Re, 62·6; F, 23·2%. Tungsten present).

(c) *As* (*b*), *but in the presence of a five-fold excess of tungsten hexafluoride.* The reaction was less vigorous than in the previous experiments, and the carbonyl was attacked slowly. As the concentration of the rhenium hexafluoride increased owing to the steady loss of tungsten hexafluoride (b. p. 19°) by evaporation, the colour of the solution changed from yellow through brown to apple-green. No oxytetrafluoride was formed; when the excess of the hexafluorides had been pumped off, the green residue was heated to 120°; yellow-green pentafluoride then distilled (Found: Re, 66·5; F, 34·0%). The brown, non-volatile residue contained rhenium and tungsten.

Action of Molybdenum Carbonyl on Rhenium Hexafluoride.—Molybdenum carbonyl dissolved in liquid rhenium hexafluoride with the formation of rhenium oxytetrafluoride, rhenium pentafluoride, and molybdenum pentafluoride. The brown residue contained molybdenum and rhenium.

Hydrolysis of Rhenium Pentafluoride.—Rhenium was estimated (*a*) in the precipitate, (*b*) in the filtrate before treatment (giving per-rhenate), and (*c*) in the filtrate after exaporation to dryness and fusion with sodium hydroxide (giving per-rhenate + fluororhenate) [Found: Re (*a*), 23·7; (*b*), 23·6; (*c*), 42·8. Calc: 22·1; 22·1; 44·2% respectively).

Thermal Decomposition of Rhenium Oxytetrafluoride.—The black residue left on pyrolysis of the oxytetrafluoride at 250° was *rhenium oxytrifluoride* (Found: Re, 71·5; F, 21·6. ReOF$_3$ requires Re, 71·8; F, 22·0%).

Thermal Decomposition of Rhenium Pentafluoride.—The pale blue residue from pyrolysis of the pentafluoride at 240° was *rhenium tetrafluoride* (Found: 71·1; F, 29·0. ReF$_4$ requires Re, 71·0; F, 29·0%).

Analyses.—Rhenium was estimated as nitron per-rhenate, and fluorine volumetrically after distillation from sulphuric acid and precipitation as lead chlorofluoride.

Physical Properties.—B. p.s were determined by Siwoloboff's method. Magnetic measurements were by Gouy's method in the temperature range 80—300° K. Since the compounds are unstable in air, the powdered specimens were introduced into "Pyrex" tubes (whose diamagnetism had previously been determined) under vacuum. Results are given in Table 3.

TABLE 3. *Corrected molar susceptibilities.*

Rhenium pentafluoride			Rhenium oxytetrafluoride		
Temp. (°K)	$10^6\chi$A	μeff.	Temp. (°K)	$10^6\chi$A	μeff.
295·0	835	1·41	294·6	748·5	1·33
272·0	864	1·38	270·0	807·7	1·32
249·0	887	1·33	250·0	873·5	1·31
231·0	905	1·30	222·0	948·5	1·30
210·0	940	1·26	198·0	1047	1·29
191·0	952	1·21	175·0	1166	1·28
170·0	971	1·15	152·0	1303	1·26
149·5	996	1·09	130·0	1480	1·24
129·5	1024	1·01	106·4	1762	1·23
110·5	1049	0·97	84·1	2170	1·21
105·0	1067	0·95			
	$\theta = 580°$			$\theta = 34°$	

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