526. *Two Fluorides of Osmium.*

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Reduction of osmium hexafluoride yields the pentafluoride and the tetrafluoride. The magnetic moment of osmium pentafluoride has been determined.

ALTHOUGH recent work has fixed the formula of the highest fluoride of osmium [1,2] and has elucidated the nature of some of the fluorine compounds of iridium [3] and platinum,[4,5] the fluorine compounds of the platinum metals remain a little known and difficult field of study.

Since the volatile fluoride of osmium has proved to be a hexafluoride and not an octafluoride, it follows that the materials to which Ruff [6] ascribed the formulæ OsF_6 and OsF_4 do not have these compositions and require to be re-examined in the light of the new evidence. The reduction of the hexafluoride of the neighbouring element, rhenium, by metallic carbonyls has recently been studied in these laboratories [7] and we now report the application of a similar technique to osmium hexafluoride. In the course of this work two lower fluorides of osmium have been isolated. Osmium pentafluoride, OsF_5, appears to be the same substance as Ruff's " OsF_6 " but our osmium tetrafluoride has quite different properties from the substance of the same composition reported by Ruff and must be considered as a new compound.

Osmium Pentafluoride.—Tungsten carbonyl reacts vigorously with osmium hexafluoride at 0° and carbon monoxide is evolved. In the presence of excess of hexafluoride a grey-green suspension remains below a green solution when the temperature is raised above the melting point of OsF_6. After the volatile hexafluorides of osmium and tungsten (the latter is formed during the reaction) have been pumped off, a grey-green mixture of osmium pentafluoride, osmium tetrafluoride, and osmium metal remains which is separated by fractional distillation under a vacuum.

Osmium pentafluoride is a blue-grey crystalline solid which melts at 70° to a green, viscous liquid which does not easily recrystallise when cooled below the melting point. The liquid changes colour reversibly as the temperature is raised and at the boiling point (233°) * is bright blue. The vapour is colourless. Osmium pentafluoride can be handled and stored in glass under rigorously dry conditions, but in the atmosphere it blackens at once, attacks glass, and evolves osmium tetroxide. The compound dissolves exothermally in water to give a brown solution and a small precipitate of hydrated osmium dioxide. As with ReF_5, some of the fluorine is retained in a complex fluoro-ion. Some tetroxide is also formed. Debye *X*-ray powder photographs, from their complexity, indicate a low crystal symmetry, and the magnetic behaviour of the pentafluoride is unusual (see Table).

Magnetic moment of osmium pentafluoride.

Temp. (°K)	$10^6\chi_A$	$\mu_{eff.}$ (B.M.)	Temp. (°K)	$10^6\chi_A$	$\mu_{eff.}$ (B.M.)	Temp. (°K)	$10^6\chi_A$	$\mu_{eff.}$ (B.M.)
295·4	1770	2·06 *	209·5	2320	1·98	129·5	3180	1·82
271·5	1900	2·04	190·0	2490	1·95	112·0	3400	1·75
249·0	1980	2·02	170·0	2680	1·92	101·5	3640	1·73
230·0	2170	2·00	149·0	2190	1·87			

* $\mu'_{eff.}$ (B.M.) 2·31.

Osmium pentafluoride is prepared in two other ways. Iodine reduces osmium hexafluoride quantitatively to OsF_5 in iodine pentafluoride solution provided the hexafluoride

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* By direct measurement. From measurements of vapour pressure (by G. B. H.), the b. p. is 225·5°.

[1] Weinstock and Malm, *J. Amer. Chem. Soc.*, 1958, **80**, 4466.
[2] Hargreaves and Peacock, *Proc. Chem. Soc.*, 1959, 85.
[3] Robinson and Westland, *J.*, 1956, 4481.
[4] Weinstock, Claussen, and Malm, *J. Amer. Chem. Soc.*, 1957, **79**, 5832.
[5] Bartlett and Lohmann, *Proc. Chem. Soc.*, 1960, 14.
[6] Ruff and Tschirch, *Ber.*, 1913, **46**, 929.
[7] Hargreaves and Peacock, *J.*, 1960, 1099.

is in excess: $10OsF_6 + I_2 \longrightarrow 10OsF_5 + 2IF_5$. If sufficient iodine is present the reaction goes further and a black, non-volatile solid is formed with a composition near that of an iodotetrafluoride $OsIF_4$.

Irradiation of the hexafluoride with ultraviolet light at 25° gives solid pentafluoride and free fluorine. After a time, if the photolysis is carried out in a closed vessel, no more pentafluoride is formed even though some of the hexafluoride is still present, showing that the system has reached a stationary state.

Osmium Tetrafluoride.—A small amount of the tetrafluoride, mixed with metallic osmium, is left behind when the residue from the osmium hexafluoride–tungsten carbonyl reaction has been warmed to 120° under a good vacuum to remove the pentafluoride. When the temperature is raised to 280—300° the tetrafluoride distils as a yellow, viscous liquid. The liquid sets below 200° to a glass which crystallises with great difficulty. The partially crystalline material melts at about 230°. The compound is sensitive to moisture and dissolves in water to form a clear yellow solution.

Discussion.—The properties of osmium pentafluoride are sufficiently close to those of Ruff's " OsF_6 " to be sure that they refer to the same substance. The chief difference, the greater reactivity of Ruff's compound towards glass and silica, is clearly due to the presence of moisture or hydrogen fluoride in his material. We have not obtained any of the black material which Ruff claimed to be the tetrafluoride, but the properties he ascribes to it might be expected for an oxydifluoride or a trifluoride.

Liquid osmium pentafluoride, like the other transition-metal pentafluorides, is viscous just above its melting point and must be highly polymerised. The distinct and characteristic change of colour as the temperature is raised is presumably connected with the breaking down of the polymeric chains or rings.

The effective magnetic moment of the solid is very much smaller than that required for 3 unpaired spins (3·88 B.M.), and a simple 5-covalent molecular structure is ruled out. Whether the quenching takes place owing to metal–fluorine–metal links or direct metal–metal bonds is an interesting question but the answer will have to await a complete structural determination.

Osmium tetrafluoride has properties which lie between those of the surprisingly volatile iridium tetrafluoride and the involatile platinum tetrafluoride. No detailed comparison is possible because of our slight knowledge of the compounds, especially of platinum tetrafluoride which has obviously been frequently confused in the past with PtF_5. So far as external appearance goes there is a break in properties between these three compounds and the tetrafluorides of the neighbouring elements rhenium and rhodium which may well be a reflection of a change in structural type.

EXPERIMENTAL

Reagents.—Osmium hexafluoride and iodine pentafluoride were prepared from the elements. Tungsten hexacarbonyl (from V. A. Howe and Co., Limited, London) was resublimed under a vacuum before use. During the preparation of the osmium hexafluoride the concurrent formation of a very small amount of a golden-yellow solid (subliming at 90° in a vacuum) was noticed (cf. $PtOF_4$ [5]). This material was blackened by moisture and dissolved in water to give a black precipitate and a yellow solution. The osmium content was near that required by the oxytetrafluoride (Found: Os, 67·0. Calc. for $OsOF_4$: Os, 67·4%).

Reduction with Tungsten Carbonyl.—Excess of osmium hexafluoride was condensed in a reaction bulb containing a weighed quantity of tungsten carbonyl. The bulb was allowed to warm so that the hexafluoride just began to melt. At this stage a vigorous reaction set in which was controlled by judicious use of a vacuum flask containing liquid oxygen. When reaction was complete, the volatile hexafluorides were pumped off and the apparatus was kept under a high vacuum while the temperature was gradually raised. At 120° a blue-green liquid appeared above the surface of the hot bath. This was collected in a separate vessel and proved to be *osmium tetrafluoride* (Found: Os, 66·5; F, 33·4. OsF_5 requires Os, 66·7; F, 33·3%). At 280—300° a little *osmium tetrafluoride* distilled (Found: Os, 71·7; F, 26·3%). OsF_4 requires

Os, 71·5; F, 28·5%). The remaining grey-black solid in the bulb contained little fluorine and was shown to be metallic osmium by a Debye *X*-ray powder photograph.

Reduction with Iodine.—Excess of osmium hexafluoride and five times the volume of iodine pentafluoride were condensed on a weighed quantity of iodine in a borosilicate-glass bulb. The bulb was allowed to reach room temperature in order to start the reaction, which was completed by warming to 50°. After the excess of osmium hexafluoride and iodine pentafluoride had been pumped off, the green pentafluoride was purified by vacuum-distillation (Found: Os, 67·1; F, 32·8%). If the hexafluoride was not in excess the product contained iodine, and when a large excess (100%) of iodine over osmium hexafluoride was used the product had a composition approaching that of $OsIF_4$ (Found: Os, 50·5; I, 34·7; F, 19·6. Calc. for $OsIF_4$: Os, 48·4; I, 32·3; F, 19·3%).

Photolysis.—Osmium hexafluoride (2 g.) in an evacuated silica bulb was irradiated at 25° with ultraviolet light. In a few hours it was coated with grey crystals whose quantity did not perceptibly change with further exposure. This proved to be OsF_5 (identified by its physical properties). The liberated fluorine was identified by its smell and chemical properties.

Magnetic Moment.—The moment of osmium pentafluoride was determined by the Gouy method. The powdered solid was introduced into the sample tube in a dry-box.

Debye X-*Ray Photographs.*—Specimens were mounted in evacuated Pyrex capillaries and photographed in Cu-K_α filtered radiation on a 19 cm. camera.

Analyses.—Compounds were decomposed in saturated sodium hydrogen carbonate solution. Osmium was precipitated as a mixture of metal and dioxide by hydrazine hydrate in alkaline solution and estimated as metal after filtration and reduction. This method was tedious but reliable. Fluorine was determined in the filtrate from the osmium determination by distillation of an aliquot part followed by precipitation as lead chlorofluoride and titration of the chloride equivalent by the Volhard procedure. Iodine was determined gravimetrically as silver iodide.

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