963. *Chemical Properties of Tungsten Hexafluoride.*

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Pure tungsten hexafluoride does not react with alkali-metal fluorides under strictly anhydrous and grease-free conditions. With sulphur trioxide a fluorosulphate, $WF_2(SO_3F)_4$, is formed. New addition compounds of tungsten hexafluoride with ammonia, pyridine, and methylamine are described.

As molybdenum hexafluoride[1] and vanadium pentafluoride,[2] after careful purification, can be satisfactorily studied in grease- and moisture-free glass apparatus, we examined some reactions of tungsten hexafluoride under similar conditions. That association followed by self-ionisation is less likely in tungsten hexafluoride than in the liquid pentafluorides of the Group VA elements is suggested by the normal value of Trouton's constant[3] (21·5) as compared with the abnormally high values of 33·1 and 25·4 found for vanadium[2] and niobium pentafluorides[4] respectively.

Previous investigations of tungsten hexafluoride[5,6] have been largely qualitative and

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[1] O'Donnell, *J.*, 1956, 4681.
[2] Clark and Emeléus, *J.*, 1957, 2119.
[3] Ruff and Ascher, *Z. anorg. Chem.*, 1931, **196**, 413.
[4] Fairbrother and Frith, *J.*, 1951, 3051.
[5] Ruff and Eisner, *Ber.*, 1905, **38**, 742.
[6] Priest and Schumb, *J. Amer. Chem. Soc.*, 1948, **70**, 2291.

many reaction products have not been identified. Cox, Sharp, and Sharpe [7] claimed that the hexafluoride is absorbed by alkali-metal fluorides to form the octafluorotungstates, M_2WF_8, but they were unable to use pure tungsten hexafluoride since their samples, prepared from bromine trifluoride and tungsten metal, were contaminated with bromine. Also their apparatus contained vacuum grease which may have reacted slowly with the hexafluoride. These reactions with alkali-metal fluorides have been re-examined and, contrary to the earlier results, tungsten hexafluoride was found not to combine with potassium or cæsium fluorides at room temperature, provided that all materials and apparatus were completely dry. Absorption of the hexafluoride was observed when insufficiently dried samples of potassium or cæsium fluorides or potassium hydrogen difluoride were used, but even in these cases it was not rapid. The products were probably mixtures of the alkali-metal oxyfluorotungstates and acid fluorides. Since the presence of bromine possibly caused the reactions previously reported, the action of tungsten hexafluoride with dry potassium and cæsium fluorides in the presence of free bromine was investigated; there was no reaction. It thus appears that pure tungsten hexafluoride does not react with the alkali-metal fluorides at room temperature, although the possibility of combination's occurring under different, as yet unknown, conditions is not eliminated.

Tungsten hexafluoride resembles niobium pentafluoride in virtually not reacting with sulphur dioxide at room temperature, although on long standing traces of thionyl fluoride and tungsten oxyfluoride are formed. With sulphur trioxide it forms the compound $WF_6,4{\cdot}5SO_3$, which can probably be formulated as the fluorosulphate $WF_2(SO_3F)_4$. Like the corresponding niobium and tantalum pentafluoride derivatives, $NbF_3(SO_3F)_2$ and $TaF_3(SO_3F)_2$, this is an involatile, viscous liquid which fumes in air and is vigorously hydrolysed by water. The discrepancy in the analytical figures is attributable to the difficulty of removing excess of sulphur trioxide. Four moles of sulphur trioxide react with each mole of hexafluoride, whereas with the niobium and tantalum compounds two moles of sulphur trioxide react per mole of pentafluoride. This may be related to the fact that tungsten hexafluoride can lose up to four fluorine atoms to form the oxyfluorides WOF_4 and WO_2F_2, while the Group VA pentafluorides form only one series, MOF_3. All the reactions of tungsten hexafluoride so far discussed show considerable differences from those of vanadium pentafluoride.[8]

The reaction of tungsten hexafluoride with anhydrous ammonia was studied by Ruff and Eisner,[5] who reported the formation of an orange-brown solid with gaseous ammonia and of a white solid with liquid ammonia; neither product was identified. The orange-brown solid has now been shown to be tetramminohexafluorotungsten(VI), $(NH_3)_4WF_6$. This was the only product with gaseous or liquid ammonia and the reported formation of a white solid was not confirmed. Tetramminohexafluorotungsten(VI) is hygroscopic, turns white in air, and dissolves in water to a purple solution which fairly rapidly becomes colourless in air. The compound thus seems similar to the ammonia derivative of tungsten oxytetrafluoride, $2WOF_4,NH_3$.[9]

With pyridine a similar type of addition compound, tripyridinehexafluorotungsten(VI), $(C_5H_5N)_3WF_6$, is formed. This is a white, hygroscopic solid which dissolves instantly in water with the formation of a similar transient purple colour. The origin of this colour is not clear, but titration of the purple solutions with oxidising agents showed that it was not due to lower valence states of tungsten. Attempts to convert tripyridinehexafluorotungsten(VI) into the pyridinium salt resulted in hydrolysis and the formation of oxyfluorotungstate and tungsten trioxide. This is to be expected in view of the doubtful existence of complex fluorides derived from tungsten hexafluoride.

Tungsten hexafluoride forms tri(methylamine)hexafluorotungsten(VI), $(CH_5N)_3WF_6$,

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[7] Cox, Sharp, and Sharpe, *J.*, 1956, 1242.
[8] Clark and Emeléus, *J.*, 1957, 2119.
[9] Ruff, Eisner, and Heller, *Z. anorg. Chem.*, 1907, **52**, 256.

by reaction with dry methylamine. This is a white, hygroscopic solid, less stable than the pyridine derivative, and its aqueous solution also shows a transient purple colour.

EXPERIMENTAL

Tungsten hexafluoride was provided by the United Kingdom Atomic Energy Authority, whom we thank. Preliminary molecular-weight measurements showed it to be contaminated with hydrogen fluoride which was removed by passage through four tubes containing dry sodium fluoride. Its purity was determined by molecular-weight measurements in the apparatus described previously [1] and by analysis for tungsten by the cinchonine hydrochloride method and ignition to tungsten trioxide and, for fluorine, by precipitation as calcium fluoride (Found: W, 61·6; F, 38·3%; *M*, 298. Calc. for WF_6: W, 61·8; F, 38·2%; *M*, 298). The high-vacuum techniques previously described [1, 2] were used throughout. Since tungsten hexafluoride is somewhat less reactive than vanadium pentafluoride, we could sometimes use systems in which metal Hoke valves replaced glass taps, or capillaries and break-seals. Care was taken to dry thoroughly all apparatus by flaming *in vacuo*.

Reaction of Tungsten Hexafluoride with Alkali-metal Fluorides.—Potassium fluoride (0·323 g.), dried *in vacuo*, was treated with excess of the hexafluoride at room temperature. After 15—30 min. the hexafluoride was pumped off. The residue weighed 0·312 g. In a similar experiment with excess of bromine the initial and final weights were 0·270 and 0·272 g. In neither case did the recovered fluoride contain tungsten. Damp potassium fluoride (0·201 g.) gave a residue weighing 0·277 g. after treatment with hexafluoride as above. A sample of undried potassium hydrogen difluoride (0·320 g.) increased in weight by 0·030 g. when similarly treated. Cæsium fluoride (0·283 g.), when treated as above with tungsten hexafluoride, gave a residue (0·282 g.) which was free from tungsten. A second sample (0·257 g.), which was not dry, increased in weight to 0·325 g. (Found: W, 15·3; F, 18·8. Calc. for Cs_2WF_8: W, 36·5; F 30·2%). In the reactions in which dry samples were used the glass was not etched. The purity of recovered hexafluoride was checked by molecular-weight measurements.

Reaction with Sulphur Dioxide.—Excess of dry sulphur dioxide was allowed to react with tungsten hexafluoride at room temperature for 24 hr. The volatile products were separated into fractions condensing at −78°, −112°, and −196°, leaving a small amount of an involatile, white solid. The −78° fraction was unchanged tungsten hexafluoride (Found: *M*, 296. Calc. for WF_6: *M*, 298), while the −112° fraction was sulphur dioxide (Found: *M*, 68·2. Calc. for SO_2: *M*, 64·0). The very small amount of material (0·015 g.) condensed at −196° was thionyl fluoride (Found: *M*, 86·1. Calc. for SOF_2: *M*, 86·0). The involatile white solid had a tungsten : fluorine ratio of 1 : 3·92 and was tungsten oxyfluoride, WOF_4.

Reaction with Sulphur Trioxide.—Tungsten hexafluoride and sulphur trioxide reacted slowly at room temperature forming, after several hours, a clear, viscous liquid. By heating the reaction trap to 50° *in vacuo* for several hours, all volatile substances were distilled off, but most of the product was involatile under these conditions. The small amount of volatile products was mainly excess of sulphur trioxide. The viscous liquid fumed in air and reacted vigorously with water, precipitating yellow tungsten trioxide. The *compound* gave analytical results corresponding to $WF_6,4{\cdot}5SO_3$ (Found: W, 28·0; SO_3, 54·7. $WF_6,4{\cdot}5SO_3$ requires W, 28·1; SO_3, 54·7%).

Reaction with Ammonia.—Gaseous ammonia was thoroughly dried over sodium and was then condensed in excess on tungsten hexafluoride. On warming to −64° a vigorous reaction occurred with the formation of an orange-brown solid. The mixture was kept for 2 hr. at −64°, after which the only remaining volatile material was excess of ammonia (Found: *M*, 17·1. Calc. for NH_3: *M*, 17·0). The orange-brown solid was *tetramminohexafluorotungsten*(VI) [Found: W, 49·0; F, 30·4; N, 15·2. $(NH_3)_4WF_6$ requires W, 50·3; F, 31·2; N, 15·3%].

Reaction with Pyridine.—Removal of excess of dry pyridine from its reaction mixture with tungsten hexafluoride, after reaction at room temperature for several hours, left an involatile, hygroscopic white solid which dissolved instantly in water giving a purple solution. This colour disappeared on standing. The white solid was *tripyridinehexafluorotungsten*(VI) [Found: W, 34·1; F, 21·8; C, 33·6; H, 2·6; N, 7·8. $(C_5H_5N)_3WF_6$ requires W, 34·4; F, 21·3; C, 33·7; H, 2·8; N, 7·9%]. Treatment of this compound with concentrated aqueous hydrofluoric acid gave a mixture of tungsten trioxide and oxyfluorotungstate.

Reaction with Methylamine.—Tungsten hexafluoride and dry methylamine reacted at −46° to give an involatile, white solid. The only volatile compound was excess of hexafluoride

(Found: *M*, 297). The white solid was extremely hygroscopic and produced a solution, initially purple but turning colourless on standing. Analysis showed the compound to be *tri(methylamine)hexafluorotungsten*(VI) [Found: W, 47·4; F, 28·7. $(CH_3NH_2)_3WF_6$ requires W, 47·1; F, 29·2%].

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