126. *Reactions of Iodine Pentafluoride with Inorganic Substances. Iodine Oxytrifluoride and Iodyl Fluoride.*

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The reactions of iodine pentafluoride with typical oxides, salts, and metals are described. They lead to a number of new compounds many of which are of a molecular type. A straightforward method of preparing iodine oxytrifluoride is given and the reactions involved are made clear. Thermal decomposition of this compound gives rise to the new iodyl fluoride, IO_2F; this can be reconverted into the oxytrifluoride by heating it with iodine pentafluoride. A study of some of these reactions and the physicochemical properties of iodine pentafluoride is still in progress.

IODINE PENTAFLUORIDE was originally prepared by Moissan (*Compt. rend.*, 1902, **135**, 563) who made a cursory and qualitative investigation of its reactions with a large number of metals. Emeléus and Sharpe recently (*J.*, 1949, 2206) focused attention on the compound by preparing the polyhalide KIF_6, and showing the probable existence of an acid–base system in this solvent similar to that furnished by bromine trifluoride (Woolf and Emeléus, *J.*, 1949, 2865). In the same laboratory, Woolf (*J.*, 1950, 3678) showed that iodine pentafluoride reacts with antimony pentafluoride to give $SbIF_{10}$, with sulphur trioxide to give a constant-boiling mixture $IF_5,1{\cdot}17SO_3$, and with potassium metaphosphate, persulphate, and iodate to give $KPO_3,2{\cdot}3IF_5$, $K_2S_2O_8,1{\cdot}02IF_5$, and $KIO_3,0{\cdot}5IF_5$, respectively.

Our interest in the compound arose from a claim by Ruff and Braida (*Z. anorg. Chem.*, 1934, **42**, 220; *Angew. Chem.*, 1934, **47**, 48) to have obtained iodine oxytrifluoride from iodine pentafluoride in three ways: (*a*) as a by-product in the preparation of iodine pentafluoride from its elements, provided a little oxygen was present during the reaction, (*b*) by restricted addition of water to iodine pentafluoride, and (*c*) by reaction between iodine pentafluoride and iodine pentoxide. The second method did not appear likely to give a unique product or a mixture readily separable, but we gave extended trial to the first method, using, as a source of oxygen, the gas itself and also silica powder mixed with the iodine. In every case, even when considerable quantities were used, we got iodine pentafluoride which on distillation left a minute, white residue insufficient for identification. The fluorination of iodine pentoxide with fluorine diluted to various extents with nitrogen gave no better results; but iodine pentoxide dissolved in boiling iodine pentafluoride to a colourless solution which, on cooling to room temperature, deposited white crystals of iodine oxytrifluoride: $I_2O_5 + 3IF_5 \longrightarrow 5IOF_3$. This reaction Ruff and Braida believed to be reversible on heating, but this is not the case. It goes smoothly until all the oxide is consumed, the oxy-compound dissolving in the excess of pentafluoride. Actually, on heating the oxytrifluoride at 110° we observed a new reaction leading to the hitherto unrecorded iodyl fluoride, IO_2F: $2IOF_3 \rightleftharpoons IO_2F + IF_5$. This is an interesting change because it is reversible. When iodyl fluoride is refluxed with iodine pentafluoride it goes completely into solution, and the oxytrifluoride is recovered. The forward reaction possibly has more than a formal resemblance to the decomposition of $K^+(IF_6)^- \longrightarrow KF^+ + IF_5^-$, for it may well be that iodine oxyfluoride has the form $(IO_2)^+(IF_6)^-$ of an ionic compound.

The new iodyl fluoride is a white solid, stable in dry air, not appreciably hygroscopic but slowly evolving hydrogen fluoride on exposure to moist air. It readily dissolves in water with irreversible hydrolysis to iodic and hydrofluoric acids: $IO_2F + H_2O \longrightarrow HIO_3 + HF$. At about 220° iodyl fluoride attacks glass and iodine is liberated.

Iodine dioxide, I_2O_4, also dissolves in iodine pentafluoride with formation of the oxytrifluoride contaminated with some free iodine. In this preparation, and in that of iodine pentafluoride from its elements, the iodine pentafluoride assumes a bright blue colour, similar in shade to a dilute solution of tetramminocupric salt and quite unlike that of iodine itself in any solvent. This was casually mentioned by Ruff and Braida (*loc. cit.*). We have found that it is not due to iodine itself, which when added to iodine pentafluoride gives a chocolate-brown solution. From such a solution, however, it can be formed by addition of a certain amount of fluorine. but the colour is discharged by the slightest excess of fluorine beyond that point : efforts to concentrate it have been unsuccessful. We incline to the view that it is a lower fluoride of iodine, subject to autoxidation even at very moderate concentrations to the pentafluoride, and completely obscured by the presence of traces of free iodine. We think it may be iodine trifluoride, IF_3, and that it may form an intermediate stage in fluorination to the pentafluoride, just as that compound is a step on the road to the heptafluoride.

We have also found that phosphorus and vanadium pentoxides, and chromium and tungsten trioxide dissolve freely in hot iodine pentafluoride, and we have isolated POF_3, VOF_3, CrO_2F_2, and $WO_3,2IF_5$ respectively, from these reactions. Molybdenum trioxide proved to be less soluble and gave $2MoO_3,3IF_5$, whereas arsenic pentoxide was insoluble; but the latter takes up iodine pentafluoride to give a bulky white solid of indefinite composition. Although antimony pentoxide dissolved freely, the residue left after evaporation required to be heated to 170° under reduced pressure before the last traces of solvent were removed : the final residue corresponded to SbF_5,IO_2F.

Neither carbon monoxide nor sulphur dioxide reacted with iodine pentafluoride, but nitrogen dioxide dissolved readily and the solution yielded a deep cream-coloured, crystalline solid IF_5,NO_2. This compound sublimes unchanged when gently heated, but higher temperatures lead to its decomposition with liberation of nitrogen dioxide. It evidently has a slight vapour pressure of NO_2 for the presence of that gas is discerned after the material has been sealed in an evacuated tube for some time. Dilute potassium hydroxide rapidly attacks it with formation of iodate and fluoride ions and liberation of some brown fumes.

As mentioned above, Woolf (*loc. cit.*) showed that certain salts, both those insoluble and those soluble in that liquid, form addition compounds with iodine pentafluoride. We have shown that potassium periodate freely dissolves in boiling iodine pentafluoride without trace of decomposition and that the solution deposits colourless, cubic crystals of KIO_4,IF_5 on cooling. The reaction of the liquid with nitrates is very selective. For instance, potassium nitrate is decomposed by boiling iodine pentafluoride which expels the acid radical—brown fumes may be seen—and converts the whole of the potassium into the iodohexafluoride, KIF_6, first isolated by Emeléus and Sharpe (*loc. cit.*). Barium and silver nitrates, on the other hand, were insoluble but both retained some pentafluoride in the residues recovered, $Ba(NO_3)_2,2{\cdot}5IF_5$ and $AgNO_3,0{\cdot}1IF_5$.

We did not expect any reaction with the more noble metals and, indeed, silver was untouched, but following up Moissan's observation (*loc. cit.*) of a slight attack on mercury, we have found that that metal is slowly dissolved, with separation of a light brown solid $Hg(IF_5)_2$. This substance changes slowly from buff to red on exposure to air; in water it does not dissolve but slowly hydrolyses; in sodium hydroxide solution decomposition is rapid and results in a precipitate of yellow mercuric oxide and a solution containing iodate and fluoride ions. Metallic cadmium by contrast is converted into fluoride with the consequent liberation of iodine.

EXPERIMENTAL

Iodine Oxytrifluoride.—About 10 g. of iodine pentafluoride, prepared by burning dry iodine in fluorine–nitrogen (40 : 60, by vol.), was fractionated in a vacuum to free it from fluorine and heptafluoride, and was condensed, under the same conditions, on to 0·25 g. of iodine pentoxide. Dry nitrogen was admitted to atmospheric pressure and the mixture was heated to its b. p. When saturated with pentoxide, the solution was separated from the residue, which was filtered off through a sintered-glass filter incorporated in the apparatus. When the clear, colourless solution was cooled, white needles of *iodine oxytrifluoride* separated. The mother-liquor was removed by decantation, and the excess of iodine pentafluoride under vacuum at room temperature (1½ hr.) (Found : I, 64·0; F, 28·0. IOF_3 requires I, 63·6; F, 28·5%).

Iodyl Fluoride.—Iodine oxytrifluoride, when heated to 110° in the presence of dry nitrogen, fell to a white powder, and elsewhere in the apparatus iodine pentafluoride collected. To remove the last trace of the latter, the solid was kept at 110°, the vessel being subjected to continuous exhaustion, for an hour. The residual *iodyl fluoride* was a fine white powder (Found : I, 71·0; F, 10·75. IO_2F requires I, 71·3; F, 10·7%).

Iodyl fluoride (1 g.) when refluxed with iodine pentafluoride for several hours, dissolved to a colourless solution which, on cooling, deposited white, needles. The excess of iodine pentafluoride was removed by pouring off and by prolonged pumping at room temperature. The crystals were iodine oxytrifluoride (Found : I, 63·1; F, 28·3%).

When heated to 220°, iodyl fluoride loses iodine and considerably attacks glass. It is not appreciably hygroscopic, but on long storage in moist air hydrogen fluoride is slowly evolved. Water readily and quietly dissolves it to form iodic and hydrofluoric acids; and sodium hydroxide solution converts it into the alkali iodate and fluoride. When the solid is added to silver nitrate solution, silver iodate is precipitated and silver fluoride left in solution. Iodyl fluoride does not attack boiling chloroform or carbon tetrachloride; it darkens pyridine slightly and liberates iodine in contact with acetyl chloride at temperatures as low as −15°.

Reactions of Iodine Pentafluoride with Oxides.—Nitrogen dioxide. Nitrogen dioxide was absorbed at the surface of liquid iodine pentafluoride, which became first pale and then deep yellow. A solid began to crystallise on the walls of the vessel and, with the continued passage of gas, the liquid was almost completely converted into a solid. The current of nitrogen dioxide was stopped, the excess of iodine pentafluoride pumped off, and the solid dried at 100°, forming a deep cream-coloured, granular powder. It was the molecular *compound* IF_5,NO_2 (Found : I, 47·6; F, 34·6; NO_2, 17·6. IF_5,NO_2 requires I, 47·4; F, 35·4; NO_2, 17·2%). The compound sublimed when gently heated but decomposed at higher temperatures, liberating nitrogen dioxide. It had a distinct vapour pressure of nitrogen dioxide at room temperature for, on storage for a few weeks in a sealed glass tube under a vacuum, brown fumes appeared. Dilute potassium hydroxide reacted vigorously with it to form iodate and fluoride, some of the nitrogen dioxide escaping even through the alkaline solution. For analysis, the tube containing the compound had to be broken in a stoppered bottle containing the alkali.

Phosphoric oxide. Phosphoric oxide (0·15 g.) in iodine pentafluoride (10 g.) showed no change at room temperature but dissolved on gentle warming to a clear, colourless solution. No gas was evolved. On cooling, no solid separated until some of the iodine pentafluoride had been evaporated (at 5 mm. pressure). This solid, a fine white powder, proved to be iodine oxytrifluoride contaminated with a small amount of a phosphorus compound (Found : I, 59·2; F, 26·95; P, 1·80; total, 97·95%; I : F = 1 : 3·03). If, as is possible, the contaminant was phosphorus oxytrifluoride, the phosphorusf ound would indicate that it was present to the extent of about 6%. Allowance for this would require I, 59·7; F, 26·8%, in good agreement with the analytical results.

The liquid distillate was unchanged iodine pentafluoride with about 98·2% of the phosphorus originally present. We believe that the oxytrifluorides of both phosphorus and iodine are formed in accordance with the reaction : $P_2O_5 + 3IF_5 \longrightarrow 2POF_3 + 3IOF_3$. Although phosphorus oxytrifluoride is a gas (b. p. −38·8°) it remained in solution in the iodine pentafluoride, possibly, like vanadium (see below), forming a weakly linked molecular compound of POF_3 and IF_5 stable only in solution. When the mixture is distilled under reduced pressure, the compound is decomposed, giving a distillate of phosphorus oxytrifluoride dissolved in iodine pentafluoride and leaving a residue of solid iodine oxytrifluoride contaminated with a few units % of phosphorus oxytrifluoride.

Vanadium pentoxide. The oxide (0·2 g.), refluxed with iodine pentafluoride (10 g.) for 1 hour, gave a colourless solution which, on cooling, deposited a light yellow solid. The excess of pentafluoride was removed at 20°/3 mm. until the *complex* attained a constant weight (Found : V, 11·9; I, 45·9; F, 33·0. $2VOF_3,3IOF_3$ requires V, 12·0; I, 44·9; F, 33·6%).

Arsenic pentoxide. This solid increased appreciably in bulk when refluxed with iodine pentafluoride, but little of it appeared to dissolve. The residue from different experiments was far from constant in composition (Found, in two samples : As, 35·6, 20·6; I, 35·1, 40·9; F, 9·8, 10·5%).

Antimony pentoxide. The oxide (0·08 g.) slowly dissolved in hot iodine pentafluoride (10 g.). A temperature of 170° was necessary to remove the last traces of solvent, at which temperature the product appeared to be molten. On cooling it set to an opaque yellow solid *complex* (Found: Sb, 16·4; I, 50·9; F, 19·8. $SbF_5,3IO_2F$ requires Sb, 16·2; I, 50·7; F, 20·2%).

Molybdenum trioxide. The oxide did not dissolve but increased in bulk. After removal of the iodine pentafluoride, a white *complex* remained (Found : Mo, 21·5; I, 39·4; F, 28·6. $2MoO_3,3IF_5$ requires Mo, 20·3; I, 39·9; F, 29·9%).

Tungsten trioxide. Tungstic oxide dissolved easily in boiling iodine pentafluoride to give a slightly opalescent solution. When excess of the solvent was removed there remained a light yellow solid the composition of which moved towards $WO_3,2IF_5$ as a limit, as the temperature was raised : at 50°, 70°, 100°, and 160°, IF_5/WO_3 = 3·1, 2·6, 2·2, and 2·1, respectively. Although it appears that the compound at 160° was $WO_3,2IF_5$, it always had an excess of iodine (Found : W, 26·2; I, 41·8. $WO_3,2IF_5$ requires W, 27·2; I, 37·6%).

Chromium trioxide. Iodine pentafluoride (2 g.), heated at 100° in a sealed tube with excess of chromium trioxide, gave a reddish, volatile product which, when separated from other volatile material by repeated fractional distillation, proved to be chromyl fluoride (Found : Cr, 43·3; F, 33·0. Calc. for CrO_2F_2 : Cr, 42·6; F, 31·2%).

Reactions of Iodine Pentafluoride with Salts.—Potassium iodate. The salt (0·5 g.) readily dissolved in iodine pentafluoride (12 g.). After removal of excess of the latter at room temperature, and then at 120° under a vacuum, the viscous mass yielded a white *compound* KIO_4,IF_5 (Found : K, 8·7; I, 55·0; F, 20·9. KIO_4,IF_5 requires K, 8·6; I, 56·2; F, 21·0%).

Potassium nitrate. Potassium nitrate (0·5 g.), when boiled with iodine pentafluoride (10 g.), evolved nitrogen dioxide. The solution remaining at the end of the reaction gave, after removal of iodine pentafluoride under a vacuum at 20°, a white powder, KIF_6 (Found : K, 13·1; I, 44·5; F, 40·4, Calc. for KIF_6 : K, 13·9; I, 45·4; F, 40·7%).

Barium nitrate. Barium nitrate (0·4 g.), refluxed with iodine pentafluoride (10 g.) for 3 hours, gave no nitrogen dioxide but increased in bulk. Removal of the excess of iodine pentafluoride, at 5 mm. and room temperature, left a white solid; the increase in weight suggested formation of the *compound* $Ba(NO_3)_2,2{\cdot}5IF_5$ [Found : Ba, 16·0; N, 3·7. $Ba(NO_3)_2,2{\cdot}5IF_5$ requires Ba, 16·8; N, 3·4%].

Reaction of Iodine Pentafluoride with Mercury.—Mercury (0·15 g.), covered with iodine pentafluoride (*ca.* 10 g.) and kept at room temperature for 24 hours, developed a thin film of white solid on its surface. When heated to boiling and refluxed with frequent shaking for 5 hours, all the mercury was converted into a dense white solid. When the liquid was removed, first at 3 mm. and then by heating at 100° for a few minutes, the solid *compound* became light brown [Found : Hg, 30·6; I, 39·4; F, 29·9. $Hg(IF_5)_2$ requires Hg, 31·1; I, 39·4; F, 29·5%], and when left in the air it became red. It appeared to be insoluble in water, but after some days the liquid was decidedly acid, suggesting hydrolysis. The compound was soluble in alcohol but insoluble in chloroform, which was, however, coloured slightly purple, indicating that the pale brown colour was possibly due to a trace of free iodine. With sodium hydroxide the compound was rapidly hydrolysed, iodate and fluoride being formed in solution, and the mercury being quantitatively precipitated as yellow oxide.

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