335. *The Reaction of Fluorine with the Oxides and Oxy-compounds of Manganese and Rhenium.*

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Potassium permanganate and the oxides of manganese on reaction with fluorine yield manganese trifluoride contaminated with a little manganese difluoride. No oxyfluoride of manganese is produced in these reactions. Rhenium dioxide and potassium per-rhenate give two new oxyfluorides, rhenium oxypentafluoride, $ReOF_5$, and rhenium dioxytrifluoride, ReO_2F_3. That the highest fluoride of rhenium is ReF_6 has been confirmed. No evidence has been obtained of the previously reported oxyfluorides $ReOF_4$, ReO_2F_2, ReO_3F, and $ReOF_2$.

MANGANESE difluoride prepared by Berzelius (*Pogg. Ann.*, 1824, **1**, 24, 197), and manganese trifluoride, prepared by Moissan (*Compt. rend.*, 1900, **130**, 622), are well known. Wohler claimed to have isolated MnO_3F but his product is now believed to have been a mixture of potassium permanganate and fluoromanganite contaminated with silicon fluoride and we are left without reliable evidence for or against the existence of an oxyfluoride of manganese.

Ruff and Kwasnik (*Z. anorg. Chem.*, 1932, **209**, 113; 1934, **219**, 65) reported the preparation of rhenium hexafluoride and tetrafluoride, and claimed to have prepared rhenium oxytetrafluoride, $ReOF_4$, and rhenium dioxydifluoride, ReO_2F_2, by (*a*) the interaction at laboratory temperature of rhenium hexafluoride and silica, and (*b*) the action of a mixture of oxygen and fluorine on rhenium at 125—300°. Moreover, in the products from the interaction between rhenium hexafluoride, potassium fluoride, hydrogen fluoride, and fluorine in a silica vessel, they claimed to have found indications of rhenium oxydifluoride, $ReOF_2$, and rhenium trioxyfluoride, ReO_3F, although these were not isolated.

We describe the reactions between elementary fluorine, diluted with nitrogen, and manganous oxide, trimanganic tetroxide, manganese dioxide, potassium permanganate, rhenium dioxide, and potassium per-rhenate. In addition, we have repeated the work previously reported on the fluorides and oxyfluorides of rhenium.

Manganous oxide and trimanganic tetroxide begin to react with fluorine just below 100° and continue to do so with incandescence. The product from both oxides is mainly manganese trifluoride carrying a trace of manganese difluoride. Manganese dioxide begins to react at 150° and gives the same product. Although looked for, no oxyfluoride of manganese was found in the residue from these experiments : the only volatile products were silicon fluoride from the glass and traces of hydrogen fluoride.

Potassium permanganate begins to react at about 150° and continues with sparks and incandescence. No trace was found of any oxyfluoride of septavalent manganese, and the residue was mainly a mixture of manganese trifluoride and potassium fluoride with a little manganese difluoride. No volatile manganese compound was formed, indicating the probable absence of potassium fluoromanganite, K_2MnF_6, which volatilises when heated.

The reaction with rhenium dioxide starts at 100° and continues with incandescence (cf. MnO_2). From this reaction two hitherto unknown oxyfluorides of rhenium, *viz.*, the *oxypentafluoride*, $ReOF_5$, and the *dioxytrifluoride*, ReO_2F_3, in which rhenium exhibits its maximum valency, have been prepared.

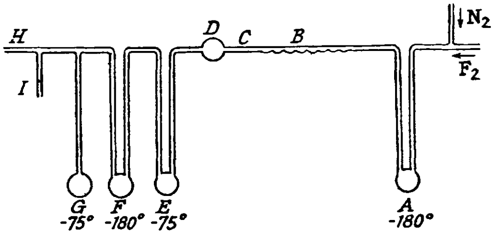
Potassium per-rhenate begins to react with fluorine at about 100°, melts with the heat of the reaction, and becomes yellow. The products are the same two new compounds, together with a residue of potassium fluoride.

In all these reactions no oxygen compound with fluorine could be detected, which suggests that in some of these reactions, *e.g.*, that involving MnO, oxygen is first liberated during the fluorination.

No evidence has been obtained of rhenium heptafluoride in the fluorination of metal, oxide, per-rhenate, or the hexafluoride, and the finding of Ruff and Kwasnik (*loc. cit.*) that the highest fluoride of rhenium is ReF_6 is confirmed. At temperatures above 300° rhenium hexafluoride undergoes disproportionation in contact with silica to yield traces of rhenium tetrafluoride. Contrary to their findings, however, pure rhenium hexafluoride does not react with silica at ordinary temperatures, nor does the reaction between rhenium, fluorine, and oxygen yield the oxyfluorides $ReOF_4$ and ReO_2F_2. The latter reaction has been carried out in vessels of Pyrex glass, nickel, and fluorite, and in each case the main reaction products were the oxypentafluoride and dioxytrifluoride. Furthermore, there were no indications of the trioxyfluoride, ReO_3F, or the oxydifluoride, $ReOF_2$, following the interaction of fluorine with a mixture of rhenium, potassium fluoride, and hydrogen fluoride in a silica vessel.

EXPERIMENTAL.

(a) *Manganese Compounds.*—The compounds to be fluorinated were dried by gently heating them in a vacuum for several hours. The reaction vessel was of Pyrex, and a mixture of fluorine and nitrogen (20 : 80, by vol.) was passed over the manganese compound at the rate of about 5 l. per hour. A liquid-air trap was inserted in the apparatus before the reaction vessel to remove traces of hydrogen fluoride. A series of three such traps was used to retain volatile products. Manganese trifluoride was principally produced (Found, in product from fluorination of manganese oxide : Mn, 49·9 ; F, 50·2. Calc. for MnF_3 : Mn, 49·1 ; F, 50·9%). The small amount of manganese fluoride always present accounts for the slightly low fluorine values.



(b) *Rhenium Compounds.*—Anhydrous rhenium dioxide was prepared by dissolving the metal in dilute hydrogen peroxide and boiling the solution to give per-rhenic acid. This was then reduced with zinc dust and hydrochloric acid, giving a precipitate of black, hydrated dioxide, $ReO_2,2H_2O$. After being collected in a sintered-glass crucible and washed with hydrochloric acid and water, it was dried at 110°. The product was then transferred to a silica tube which was attached to a drying train and Hyvac pump, and the oxide was completely dehydrated by heating the silica tube for 6 hours at 350° under constant evacuation. Any trace of rhenium heptoxide, Re_2O_7, present was removed by sublimation, a small luminous Bunsen flame being used.

The apparatus of Pyrex (see figure) was first swept clear of air with pure nitrogen, and the above fluorine–nitrogen mixture was streamed through at a rate of 5 l. per hour. Any trace of hydrogen fluoride was removed in *A*. No reaction occurred at room temperature but at about 100° the dioxide took fire and burned with the evolution of copious white fumes. It was found convenient, in view of the heat of the reaction, to divide the charge of dioxide into several small portions, each in a separate depression in the reaction vessel. Starting at the end nearest *C*, each portion was separately raised to the reaction temperature. The more volatile products collected in *E* and *F*, and the less volatile in *D*. When the reaction was finished, the fluorine was displaced by nitrogen, and the apparatus sealed at points *C* and *H*, evacuated *via I*, and finally sealed off at this point. In previous experiments attempts were made to fractionate the two substances but all the evidence pointed to the original separations being effective. The volatile products in *E* and *F* were sublimed into the vapour-density bulb *G*, which was cooled to $-75°$. Any silicon tetrafluoride (sublimes at $-90°$) present was then removed by cooling *E* or *F* to $-180°$; *G* and *D* were sealed off, and their contents analysed.

(*a*) The fraction in *G* (Found : Re, 62·8; F, 31·9%; *M*, 300·7. $ReOF_5$ requires Re, 62·7; F, 32·0%; *M*, 298·3) was ***rhenium oxypentafluoride.*** At room temperature it is a cream-coloured crystalline solid, which melts to an almost colourless liquid at 34·5°, and boils at 55°/760 mm. Its liquid density is 3·8 at 40° and its solid density is 4·2 at the m. p. In the absence of moisture it does not attack glass at ordinary temperatures if it is free from hydrogen fluoride. It gives white fumes when exposed to moist air, and dissolves in water with hissing, forming a colourless solution containing per-rhenic acid and hydrofluoric acid, $ReOF_5 + 3H_2O = HReO_4 + 5HF$. In the presence of water sexavalent rhenium would have given a black precipitate of hydrated rhenium dioxide $ReO_2,2H_2O$, *viz.*, $3Re^{6+} = 2Re^{7+} + Re^{4+}$. This rules out the possibility of our compound being a mixture of rhenium hexafluoride and oxytetrafluoride, $ReOF_4$, and points significantly to its being the oxypentafluoride, $ReOF_5$. The oxyfluoride is readily reduced (cf. ReO_2F_3 below) to Re^{4+} by traces of organic matter.

(*b*) The fraction in *D* (Found : Re, 67·0; F, 20·5. ReO_2F_3 requires Re, 67·7; F, 20·7%) was ***rhenium dioxytrifluoride.*** At room temperature it is a pale yellow powder, which begins to sinter at 90° and is definitely liquid at 95°. The vapour density at this temperature is appreciable and the compound can be distilled without decomposition in a luminous Bunsen flame at 200°. The distillate was homogeneous and each successive fraction had a composition corresponding to the formula ReO_2F_3. The liquid solidifies to a glass but the compound can be obtained crystalline by slow sublimation *in vacuo.* ReO_2F_3 does not attack glass below about 300°, and it is deliquescent in moist air. It dissolves in water to form a colourless solution containing per-rhenic acid and hydrofluoric acid, showing the presence of Re^{VII} only : $ReO_2F_3 + 2H_2O = HReO_4 + 3HF$. Unlike $ReOF_5$, it is only slowly reduced by traces of organic matter to quadrivalent rhenium. In this preparation the two oxyfluorides are produced in the proportions of about 1 part of $ReOF_5$ to 3 parts of ReO_2F_3.

Potassium per-rhenate was fluorinated in the same type of apparatus and reaction was found to begin at 100°. Under the same experimental conditions as that used for ReO_2 the same two oxyfluorides were formed in the ratio of about 1 part of $ReOF_5$ to 10 parts of ReO_2F_3.

The fluorination of rhenium metal at about 125° produced a pale yellow solid exactly resembling custard-powder in appearance. It had m. p. 19° and b. p. 48° and was identified as ReF_6 (Found : Re, 62·0; F, 38·7%; *M*, from vapour-density determination, 302·0. Calc. for ReF_6 : Re, 62·0; F, 38·0%; *M*, 300·3). This is in agreement with the findings of Ruff and Kwasnick (*loc. cit.*), who were also unable to prepare a fluoride of rhenium containing more than six atoms of fluorine.

Attempts to repeat those authors' work on the oxyfluorides of rhenium were made on the following lines. (1) Fluorine (75 parts) and oxygen (25 parts), together with a little nitrogen to act as a carrier gas, were passed over rhenium. Vessels used were Pyrex glass, nickel, and fluorite. (2) Rhenium hexafluoride was sealed up in a quartz bulb and left for several weeks at room temperature. (3) A fluorine–nitrogen stream was passed over a heated mixture of rhenium and potassium hydrogen fluoride (KF,2HF) in a silica vessel. In (1) the new compounds described above were obtained, the primary product being rhenium oxypentafluoride, $ReOF_5$, and in (2) no reaction took place. In (3) a blue-black complex residue was obtained from which no oxyfluoride of rhenium could be isolated. It was found that above 300° rhenium hexafluoride reacts with quartz yielding minute quantities of a dark green-blue solid agreeing with the description given by Ruff and Kwasnik (*loc. cit.*) for rhenium tetrafluoride, but the quantities were too small for confirmatory analysis.

The authors express their indebtedness to the General Chemicals Division of Imperial Chemical Industries Limited, Runcorn, for the fluorine cell used, and to King's College for a Post-Graduate Studentship, which enabled one of them (R. D. P.) to take part in the work.

KING'S COLLEGE, NEWCASTLE-ON-TYNE, 1. [*Received, January 30th*, 1950.]