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FLUORIDES OF HIGH OXIDISING POWER AND THEIR APPLICATION TO THE PREPARATION OF ORGANIC FLUORINE COMPOUNDS

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I. INTRODUCTION

The extraordinarily high reactivity of elementary fluorine, together with the chemical properties of organic fluorine compounds, make methods for synthesising the latter fundamentally different from those for obtaining other halogen derivatives. All methods of preparing organic fluorine compounds can be divided into four broad groups.

The first group comprises reactions of organic compounds with elementary fluorine or with fluorides of high oxidising power. These reactions are essentially oxidations, taking place by a radical mechanism, and involving either replacement of hydrogen (or halogen) by fluorine or addition of fluorine to a multiple bond.

The second group is formed by reactions involving the exchange of other halogens for fluorine by means of hydrogen fluoride or a metal fluoride possessing no oxidising power (potassium fluoride, antimony trifluoride).

In the third group of reactions functional groupings containing oxygen, sulphur, or nitrogen are exchanged for fluorine by interaction with sulphur tetrafluoride, by the Schiemann reaction, and by other methods.

The fourth group can be regarded as including the numerous reactions in which groupings containing fluorine are introduced into organic compounds containing no fluorine, by the scheme

$$R_H - X + R_F Z \rightarrow R_H - R_F + XZ,$$
$$R_{H(\text{or } F)} - CH = CH_2 + R_F - X \rightarrow R_H - \underset{X}{CH} - CH_2 - R_F.$$

The present review will cover only reagents which effect reactions of the first group, i.e. fluorides which oxidise organic compounds to organofluorine compounds. Attention will be paid primarily, not to summarising the extensive literature on the most important fluorinating agents (AgF_2, CoF_3), but to elucidating the theoretical possibility of using fluorides for this purpose as a function of the chemical properties of the element concerned and its position in the Periodic System. Higher fluorides of the transition metals and of certain elements in the main subgroups of the Periodic System are of great practical importance (in the atomic industry, as oxidants in rocket technology). Information on the fluorides of interest to us will be reported in the sequence in which the elements are arranged among groups of the Periodic System (the elements capable of forming fluorides having high oxidising power are V, Cr, Mn, Tc, Re, Ru, Os, Ni, Pd, Pt, Cu, Ag, Au, Hg, Tl, Pb, Sb, Bi, O, Po, Cl, Br, I, At, Kr, Xe, Rn, Ce, Pr, Nd, Tb, Dy, U, and Pu).

The oxidising power of these fluorides is extremely varied, and cannot yet be estimated quantitatively in any way. Considerable interest should attach, in connection with the assessment of the oxidising power of ElF_x, to the energy of formation of the El–F bonds, but unfortunately knowledge of these bond energies and of their orders is very far from what could be desired. Yet even in such a simple molecule as F_2 the order of the F–F bond is less than unity, which entails an abnormally low bond energy. The reason for such anomaly in this case has been analysed in detail by the molecular orbital method[1]. Some elements are not at all readily available, and therefore have been insufficiently investigated; while others, although readily available, have higher fluorides which cannot be purified, so that their study is difficult. The highly corrosive nature of some fluorides, which attack even polytetrafluoroethylene and platinum, make it impossible to study them by the usual methods. In this paper the assignment of some fluorides to the category of oxidising agents is made on the basis of their chemical properties, often studied quite superficially, and in some cases only on the basis of general considerations regarding their reactivity. Nevertheless, we feel that future quantitative results will hardly seriously contradict our purely qualitative considerations.

Fluorides of high oxidising power show increased stability and lower oxidising power on complex formation, which makes it possible to obtain fluorides in which the metals exhibit an abnormally high valency (Ni^{4+}, Cu^{4+}).

II. HIGHER FLUORIDES OF TRANSITION METALS

Incomplete electron levels become filled in the atoms of transition metals, which comprise elements of atomic numbers 21–30, 39–40, and 57–90 (lanthanum, lanthanides, and the series of elements from Hf to Hg), together with 89–104 (Ac, Th, Pu, U, etc.). Transition metals can utilise the electronic levels *d* (and *f* in the lanthanides and actinides) for chemical bond formation.

Fluorides of high oxidising power occur among quadrivalent derivatives of cerium, praseodymium, terbium, and dysprosium in the lanthanide subgroup of Group III in the Periodic System, and are represented by the hexafluorides of uranium, neptunium, and plutonium in the actinide subgroup.

Whereas in the vanadium subgroup only vanadium pentafluoride possesses high oxidising power, and in the zinc subgroup only mercury difluoride, in the case of chromium, manganese, iron, cobalt, nickel, and copper subgroups only iron gives no fluoride of high oxidising power.

1. Higher Fluorides of Lanthanides

The appearance in lanthanides of 4*f*-electrons, at energy levels close to those of 5*d*-electrons, makes it possible for some lanthanides to yield more or less stable quadrivalent derivatives. The stability of the quadrivalent state diminishes with increase in the number of *f*-electrons, but after $4f^7$-electrons have accumulated in gadolinium, the possibility of forming a relatively unstable quadrivalent state reappears with terbium and to some extent dysprosium.

Cerium and terbium tetrafluorides are obtained by fluorinating the trifluorides with elementary fluorine at high temperatures[2,3]. There are indications that cerium tetrafluoride can be obtained also from the trichloride[4] or the dioxide[5]. Data have been published on the lattice structures of CeF_4 and TbF_4 and on the partial pressures of fluorine over these compounds at high temperatures[3,6].

When heated in air, cerium and terbium tetrafluorides are converted into oxides. The fluorides are unchanged by cold water[2,3], but react quite rapidly even in acidified solutions of aluminium nitrate with the evolution of gaseous oxygen, TbF_4 reacting slowly even in the absence of acid[3].

Fowler used CeF_4 for the vapour-phase fluorination of hydrocarbons with the aim of obtaining perfluorinated products. Since CeF_4 was less reactive than CoF_3, fewer carbon–carbon bonds underwent cleavage, so that more viscous products of higher boiling point were obtained[9]. In the opinion of Fowler and Anderson, CeF_4 is to be preferred to other fluorinating agents if the carbon skeleton is to be obtained unchanged in vapour-phase fluorination over the temperature range 150–450°. There are indications of the use of CeF_4 to obtain partly fluorinated organic compounds[5], and of the addition of fluorine to double bonds in chlorinated alkenes by means of CeF_4.[5] The chlorine in saturated chlorofluorocarbons can be replaced under the influence of CeF_4.[5] Cerium tetrafluoride is employed for the liquid-phase stabilisation of fluorinated oils in the presence of elementary fluorine[5].

It has not yet proved possible to prepare tetrafluorides of other lanthanides[3,10,11], although it has been predicted[12] that praseodymium tetrafluoride will be relatively stable.

Fluoro-complexes are known of quadrivalent cerium[13] and praseodymium[14,15] of general formulae A_2BF_6 and A_3BF_7 (where A = Na, K, Rb, and Cs and B = Ce, Pr), and the compounds $NaPrF_5$,[16] Cs_3TbF_7,[18] Cs_3DyF_7, and Cs_3NdF_7 [18] have also been obtained. In all cases the stability of the complexes increases in the sequence Na → K → Rb → Cs. The lattice parameters and the magnetic suceptibilities of these complexes have been measured[13,14]. All these complexes have been prepared by fluorinating a mixture of salts[16] or a mixture of chlorides and the corresponding oxides[13–15,17] at high temperatures. The cerium complexes are colourless and comparatively stable, and begin to react only gradually with water and hydrochloric acid. They oxidise acidified solutions of potassium iodide; concentrated sodium hydroxide solution decomposes the complexes, with precipitation of $CeO_2.xH_2O$.[13] The colourless praseodymium complexes are reduced by water with gas evolution, and are even decomposed by moist air[14]. As was to be expected, the colourless complex of quadrivalent terbium is somewhat more stable, and does not break down in moist air, but it oxidises boiling hydrochloric acid with the evolution of chlorine. Concentrated NaOH solution decomposes Cs_3TbF_7.[17] Study of the magnetic properties and the elementary composition has proved the existence of the complexes Cs_3NdF_7 and Cs_3DyF_7.[18] The yellow complexes of Nd^{4+} and Dy^{4+} liberate iodine from acidified potassium iodide solution[18].

2. Higher Fluorides of Uranium, Neptunium, and Plutonium

The fact that 5*f*-electrons are considerably more readily removed than are the 4*f*-electrons of lanthanides makes the achievement of high valencies a characteristic feature of actinides. Thus the most stable state of thorium is quadrivalent, protactinium reaches the quinquevalent state, and uranium, neptunium, plutonium, and americium are characterised by sexivalent states. As the number of 5*f*-electrons rises, their tendency to form high valency bonds falls, and the higher valency states become less stable. Thus whereas uranium hexafluoride is fairly stable, although it is a strongly oxidising compound, plutonium hexafluoride is considerably less stable, and exhibits extremely high oxidising power, while americium hexafluoride has not yet been obtained[19]. The immense practical value of the fluorides of uranium and plutonium has resulted in an extensive literature on this question[20–22]. We shall therefore confine ourselves to a brief comparison of the properties of the hexafluorides of uranium, neptunium, and plutonium, and discuss their reactions with organic compounds. The ability of uranium hexafluoride to react with all the usual organic compounds, and the need to produce resistant materials, led to the synthesis of polytetrafluoroethylene, polychlorotrifluoroethylene, and perfluorinated oils, and was the principal reason for the vigorous development of organofluorine chemistry.

Uranium hexafluoride is a moderately strong oxidant, and can be prepared, without the use of elementary fluorine or fluorides of halogens, cobalt, or silver, by the reaction[23]

$$2UF_4+O_2=UF_6+UO_2F_2.$$

Neptunium hexafluoride[24] and especially plutonium hexafluoride[24–27] are stronger oxidising agents. Thus the latter fluorinates bromine trifluoride to bromine pentafluoride[24,27], whereas uranium hexafluoride can be obtained by treating uranium compounds with bromine trifluoride[23].

Plutonium hexafluoride readily fluorinates uranium derivatives to the hexafluoride[27]. Neptunium hexafluoride occupies an intermediate position, only partly converting bromine trifluoride into the pentafluoride[24]. All the hexafluorides are immediately hydrolysed by water, but no evolution of oxygen or oxygen difluoride was observed[28,29]. Uranium hexafluoride reacts vigorously with most organic compounds (aliphatic and aromatic hydrocarbons, alcohols, and ethers) with the evolution of hydrogen fluoride and the formation of partly carbonised substances of indeterminate composition, the uranium being converted into its tetrafluoride or oxide fluoride. Trichloroethylene instantaneously reduces uranium hexafluoride to the tetrafluoride, being converted into a mixture of compounds containing chlorine and fluorine, formed by reactions involving addition, substitution, polymerisation, and decomposition[30].

At 100–200° uranium hexafluoride is rapidly and quantitatively reduced by carbon tetrachloride to uranium tetrafluoride[31]:

$$UF_6+2CCl_4 \rightarrow UF_4+Cl_2+2CCl_3F.$$

This reaction has been carefully studied for its practical application[31]. Experiments with different proportions of the reactants showed that chlorotrifluoromethane predominated when a slight excess of carbon tetrachloride was used, whereas more trichlorofluoromethane was obtained with a large excess.

When uranium hexafluoride is dissolved in 1,1,2,2,-tetrafluoroethane, reaction becomes appreciable only after a few days. The relative stability of this solution permitted its use to study several reactions of uranium hexafluoride with ammonia and with arsenic trifluoride[20]. A solution of uranium hexafluoride in tetrachloroethane is still more stable[20]. This solution takes a few weeks to decompose, and can be used for the recrystallisation of uranium hexafluoride. On the other hand, tetrachloro-1,2-difluoroethane reacts with uranium hexafluoride quite rapidly, with the evolution of a gas which is obviously dichlorodifluoromethane[20].

Uranium hexafluoride reacts with partly fluorinated hydrocarbons, replacing the hydrogen by fluorine atoms, but is completely inert towards perfluorinated hydrocarbons and chlorofluorocarbons, which are used in various operations with the hexafluoride. On prolonged heating, amorphous carbon reduces uranium hexafluoride to the tetrafluoride, with the formation of carbon tetrafluoride and other simple fluorocarbons. The hexafluoride is insoluble in carbon disulphide, and reacts relatively slowly; with moist carbon disulphide, fluorides of sulphur are formed. Uranium hexafluoride does not interact with carbon dioxide or with mercury dicyanide[20].

Plutonium hexafluoride reacts with most organic compounds still more vigorously, but perfluorinated hydrocarbons do not interact with it, too[27].

3. Higher Fluorides of the Vanadium Subgroup

Elements of this subgroup are characterised by the presence of relatively few *d*-electrons, whose energy levels are close to those of the valency *sp*-electrons. This results in participation by the *d*-electrons in the formation of valency bonds, as a result of which the elements of the vanadium subgroup exhibit a stable higher valency of +5. With increase in atomic number the mobility of the *d*-electrons increases; this tends to stabilise the higher valency of the element. In the series vanadium–niobium–tantalum the larger the positive charge on the nucleus the more weakly are the outer electrons bound to the nucleus, the lower is the ionisation potential for detachment of the corresponding electrons, and the greater the tendency of the element to form compounds corresponding to its maximum valency. The higher fluorides of elements of this group are oxidants, their oxidising power diminishing down the group.

Vanadium pentafluoride is formed by the action of fluorine on the metal at 300°,[32] by the action of chlorine trifluoride, bromine trifluoride, or iodine pentafluoride on vanadium pentoxide[33], or by the thermal disproportionation of vanadium tetrafluoride at 650°.[32] It is a relatively weak oxidising agent, but can exchange fluorine for oxygen in inorganic compounds and for other halogens in carbon tetrahalides[34,35]. There are indications that vanadium pentafluoride reacts with ether and with toluene, but the structure of the products has not been elucidated[32]. It forms salts with ammonia and with pyridine[36]. Niobium and tantalum pentafluorides are less active as oxidising agents[35].

4. Fluorides of Chromium, Molybdenum, and Tungsten

For a long time chromium hexafluoride was not identified. Fowler and his coworkers tried to obtain higher fluorides of chromium by the interaction of fluorine with chromium trichloride and chromium sesquioxide in order to study their ability to fluorinate organic compounds, but only a mixture of volatile and non-volatile fluorides was obtained, which could not be investigated because of experimental difficulties[37]. Bright red chromium pentafluoride[39] has recently been obtained, together with a small quantity of lemon-yellow chromium hexafluoride[38], by treating chromium powder with fluorine in a nickel bomb at 200 atm and 400°.[38] The yield of the hexafluoride is increased by adding manganese powder and raising the pressure to 350 atm. Chromium hexafluoride rapidly decomposes into the pentafluoride and fluorine at temperatures as low as -100° to -80°.[38]

Molybdenum and tungsten hexafluorides, in contrast, are readily available, but exhibit relatively weak oxidising properties and have no fluorinating action[40,41]: with organic compounds they form complexes.

5. Fluorides of Manganese and Rhenium

The presence of a large number of *d*-electrons enables elements in this subgroup to exhibit various valencies (+2, +3, +4, +6, and +7), the higher valencies becoming more stable from manganese to rhenium. Manganese forms a trifluoride and a tetrafluoride. The former has been well studied, and has found practical application as an extremely effective fluorinating agent (though milder than cobalt trifluoride) for organic compounds. Manganese trifluoride is used for the preparation of perfluorinated compounds under roughly similar conditions to cobalt trifluoride, the latter being more suitable for the fluorination of products of low boiling point, whereas manganese trifluoride is more useful for high-boiling compounds, since at high temperatures it causes less cleavage of carbon–carbon bonds, though the resulting product is probably incompletely fluorinated[42–45].

Wine-red manganese trifluoride is formed by treating manganese or its salts with fluorine at 250° or by treating

manganese iodate with bromine trifluoride and heating the product to 200°.[46] The extremely active manganese tetrafluoride is obtained under more severe conditions, by fluorinating simple salts ($MnCl_2$, MnF_2, $MnSO_4$,[47] MnF_3[48]) with elementary fluorine at 400–550°. The tetrafluoride is an amorphous powder, which is fairly stable at room temperature[48].

Manganese tetrafluoride is undoubtedly more reactive than the trifluoride. The latter is decomposed by water, whereas the tetrafluoride ignites spontaneously on contact with water. The trifluoride reacts with benzene, alcohol, chloroform, ether, and turpentine only when heated to 100° and above[49]. A flash of light is seen when the tetrafluoride reacts with dry petroleum ether at room temperature[47].

Quadrivalent manganese gives two series of complex fluorides — A_2MnF_6[50–52] and $AMnF_5$[50,52] (where A = Li, Na, K, Rb, Cs) — of which the brick-red compounds of the type $AMnF_5$ are the more reactive. These complex fluorides are obtained by fluorinating salts of the type $AMn^{2+}F_3$[52] or a mixture of the simple salts[48], e.g.

$$LiF + MnF_2 \xrightarrow[350°]{F_2} LiMnF_5.$$

Potassium pentafluoromanganate can be prepared by the action of bromine trifluoride on potassium permanganate with subsequent removal of excess bromine trifluoride under vacuum at 20°.[50] It is formed also by the reaction[50]

$$4KMnO_4 + 10SeF_4 = 4KMnF_5 + 10SeOF_2 + 3O_2.$$

Pentafluoromanganates are hydrolysed by water, and form brownish-black precipitates with dilute alkalis; in air they gradually decompose. Hydrogen reduces them at 250–275°: lithium pentafluoromanganate is reduced even at 150–200°, whereas the caesium salt is incompletely reduced[52].

Technetium and rhenium give the reactive fluorine compounds technetium hexafluoride[57], rhenium hexafluoride[54,55], and rhenium heptafluoride[56,57]. The volatile hexafluorides of technetium and rhenium are formed by reaction of the metal powders with fluorine (at 400° and 420° respectively), rhenium hexafluoride being obtained also by treating powdered rhenium with chlorine trifluoride at 300°.[55] On further treatment with fluorine, 1 mole of rhenium hexafluoride absorbs a further 0.5 mole of fluorine, to give the less volatile heptafluoride[56], which is probably thermally stable[57]. The infrared spectra of technetium and rhenium hexafluorides have been recorded, and the principal thermodynamic constants obtained[53,57]. All three higher fluorides are sensitive to moisture, but can be stored in a dry Pyrex glass vessel at room temperature for a long time[53,57]. Hydrolysis of technetium hexafluoride in the presence of sodium hydroxide gives a black precipitate, which dissolves on the addition of hydrogen peroxide[53]. Its behaviour is analogous to that of rhenium hexafluoride, which disproportionates on hydrolysis, giving insoluble rhenium dioxide, rhenic acid $HReO_4^-$, and hydrogen fluoride[54].

Rhenium hexafluoride is a vigorous oxidising agent, being reduced to the tetrafluoride by hydrogen at 200°, sulphur dioxide at 400°, and carbon monoxide at 300°.[54] With alkali metals it forms complexes of the type A_2ReF_8, which are readily hydrolysed by water[58].

6. Simple and Complex Fluorides of the Iron Subgroup

Since a group of five *d*-electrons is especially stable, iron(III) fluoride does not exhibit oxidising properties[59], and dissociates only at 1000° and 15 mm in a stream of nitrogen, being converted into iron(II) fluoride[60]. Cobalt, like iron, forms both a difluoride and a trifluoride, but, in contrast to iron(III) fluoride, cobalt(III) fluoride is a strong oxidising agent.

Cobalt trifluoride can be obtained by the action of fluorine on cobalt(II) fluoride or chloride at 150°.[61] It is a pale brown powder, whose physical properties and structure have been studied in detail[61]. It dissociates appreciably into cobalt(II) fluoride and fluorine in a stream of carbon dioxide at 250°–300°, and is completely dissociated at 350°. Reaction of cobalt trifluoride with water, aqueous acids, and aqueous alkalis is accompanied by very vigorous evolution of oxygen[61]. Cobalt trifluoride is widely used for the fluorination of organic compounds with the aim of preparing perfluorinated hydrocarbons. Its use for the fluorination of hydrocarbons containing about 1–20 carbon atoms has been described.

Compounds of higher molecular weight can also be fluorinated, although very considerable difficulties are involved. The fluorination of compounds containing oxygen[62] and nitrogen[63–66] has been described, but the yields are relatively low. Fluorination with cobalt trifluoride can be effected over the range 150–400° both in the vapour phase and in inert liquid perfluorinated solvents. The manufacture of perfluorinated oils for the gas-diffusion enrichment of uranium by means of cobalt trifluoride was suggested in the USA in 1941, although the cost of manufacture was extremely high. Fluorination with cobalt trifluoride has been described in detail[67,68].

The complex K_3CoF_6 was first obtained by the anodic oxidation of cobalt(II) fluoride dissolved in hydrofluoric acid, with subsequent treatment of the resulting $CoF_3.3\frac{1}{2}H_2O$ with solid potassium fluoride at -10°.[69] The corresponding ammonium complex cannot be obtained by this method[70].

Klemm and his coworkers suggested several dry methods. The first was based on the fluorination of mixtures of cobalt(II) chloride and salts containing the cation present in the final product[71], e.g.

$$3KCl + CoCl_2 \xrightarrow{F_2} K_3CoF_6.$$

The second method consists in fluorinating with dilute fluorine a complex salt containing no fluorine; for example, K_3CoF_6 can be obtained from $K_3Co(CN)_6$.[72,73] Hoppe and Klemm have reported the use of this method to prepare complexes A_3CoF_6, where A = Li, Na, K, Rb, Cs,[72,73] Ag,[74] Ba.[75] An attempt to obtain $LaCoF_6$ by fluorinating $LaCo(CN)_6$ was unsuccessful[75].

The pure A_3CoF_6 compounds possess strong oxidising properties, being decomposed by water with the separation of a black deposit and the evolution of oxygen. With aqueous perchloric acid they evolve a gas and form a bivalent cobalt salt. These complexes oxidise hydrochloric acid and acidified potassium iodide solution[74].

The previously described[71] compound K_3CoF_7 proved[72] to have the formula K_3CoF_6. At the present time only one complex of quadrivalent cobalt is known: when Cs_2CoCl_4[72] or $Cs_2Co(SO_4)_2.6H_2O$ is fluorinated, a brownish-yellow complex Cs_2CoF_6 is obtained[72,74]. The quadrivalent cobalt compound is less stable than Cs_3CoF_6.[74] Reactions of tervalent and quadrivalent cobalt complexes with organic compounds have not been studied. The physical properties of the complexes have been described[72–76].

The higher fluorides of nickel NiF_3 and NiF_4 have not yet been described, but their complex compounds of the types A_3NiF_6 and A_2NiF_6 are known.

Higher fluorides of nickel are interesting in view of their possible occurrence in electrochemical fluorination. The electrochemical fluorination of organic compounds containing oxygen, nitrogen, or sulphur is effected by passing a direct current through their solutions in anhydrous hydrogen fluoride. When nickel electrodes are used, a voltage of ~5 V is applied to the electrolytic cell, and fluorination is accompanied by relatively little cleavage of carbon–carbon bonds. Electrochemical fluorination is undoubtedly an anodic process. It has been suggested that the higher complex fluorides of nickel are active fluorine carriers[77]. This view finds indirect confirmation in the chemistry of quadrivalent nickel complexes.

The violet complex K_3NiF_6 is formed by the fluorination of a 1 : 3 mixture of potassium chloride with nickel sulphate[78] or nickel chloride[71] in a mixture of fluorine and carbon dioxide at 320°. The corresponding sodium complex is obtained similarly (from sodium chloride or bromate and nickel sulphate). Fluorination of a mixture of ACl (where A = K, Rb, Cs) and $NiCl_2$ occurs still more readily, even at 275°, diamagnetic red complexes A_2NiF_6 being obtained[71,79].

The complex K_2NiF_6 reacts very violently with water, a gas being evolved whose odour recalls that of ozone (OF_2 ?). It is relatively stable in dry air, and does not react when heated with hydrocarbons, aniline, dimethylaniline, or acetic anhydride, but reacts vigorously with acidic substances such as acetic and decanoic acids, phenol, and sulphuric and hydrochloric acids, being converted into greyish-green nickel(II) chloride:.

$$2A{-}H + K_2NiF_6 \rightarrow [H_2NiF_6] + 2KA \rightarrow NiF_2 + 2HF + 2F.$$

It is possible that similar processes occur also in electrochemical fluorination:

1. $Ni + F^- \xrightarrow{-2e} NiF_2$,
2. $NiF_2 + 2F^- + 2NR_3^HH^+ \xrightarrow{-ne} (NR_3^H)_2NiF_6$,
3. $(NR_3^H)_2NiF_6 + nF^- \xrightarrow[-nH_2]{-ne} (NR_3^F)_2NiF_6$,
4. $(NR_3^F)_2NiF_6 + 2NR_3^HH^+ \rightarrow (NR_3^H)_2NiF_6 + NR_3^F + H^+$,
5. $(NR_3)_2NiF_6 \xrightarrow[\text{off}]{\text{current}} (NR_3)_2NiF_4 + F_2$,

   $(NR_3)_2NiF_4 + 2HF \rightleftarrows NiF_2 + 2(NR_3^H)^+F^-$.

Such a mechanism is supported by the fact that, in spite of repeated attempts, electrochemical fluorination can be accomplished only at nickel anodes, except with a considerably higher overpotential at Monel-metal anodes[80]. Still further evidence in support of this mechanism is provided by the diminished yields which one of us has observed, and the decrease in stability of electrochemical fluorination, when anodes of low-grade nickel are used[81].

7. Higher Fluorides of the Platinum Metals

Among the light platinum metals, hexafluorides have been obtained of ruthenium and rhodium. Powdered ruthenium and rhodium explode in fluorine[82,83]. Ruthenium hexafluoride is a dark brown solid melting at 54°.[82] It is less volatile than the corresponding molybdenum and technetium compounds. It reacts rapidly with Pyrex glass, and to a less extent with quartz. Ruthenium hexafluoride can be stored in a nickel vessel without decomposition for a long time[82].

Rhodium hexafluoride is a black substance (the vapour being reddish-brown), resembling ruthenium hexafluoride. It breaks down into fluorine and a lower fluoride even at room temperature[83]:

$$RhF_6 \rightarrow RhF_5 + \frac{1}{2}F_2.$$

Both ruthenium and rhodium hexafluorides are extremely reactive substances: they form complexes with xenon[84,85] analogous to $XePtF_6$.[86] The infrared spectra of these hexafluorides have been recorded, and their structure has been studied[82,83].

Ruthenium pentafluoride is formed from the elements at 300°[87] and when ruthenium dioxide is treated with fluorine or with bromine pentafluoride[88]. The dark green compound[87,89] fumes strongly in the air, and reacts violently with water, being converted into a black lower oxide of ruthenium[87]. Ruthenium pentafluoride is a vigorous oxidising and fluorinating agent, iodine being oxidised to iodine pentafluoride at 160°, and sulphur to sulphur hexafluoride at 0°. At high temperatures it converts copper and silver into fluorides, and oxidises hydrogen chloride to chlorine, but it reacts only slightly with dry benzene and toluene. The reactive complexes $ARuF_6$ evolve oxygen on interaction with water[87].

Ruthenium tetrafluoride has been obtained by reducing the pentafluoride with iodine in iodine pentafluoride solution[90]. It is a non-volatile yellow solid, which blackens in moist air, and reacts violently with water, being converted into ruthenium dioxide.

Rhodium tetrafluoride is obtained by the action of fluorine on rhodium, its trichloride, or its trifluoride at 500° or by dissolving rhodium tribromide in bromine trifluoride and then evaporating off the latter. It is a hygroscopic powder, which oxidises hydrochloric acid to chlorine; it does not react with ether or carbon tetrachloride at room temperature[91]. Complexes A_2RhF_6, which are sensitive to moisture, being violently decomposed by water with the evolution of gases, have been prepared[91].

Palladium trifluoride is obtained by the action of fluorine on the dichloride[92], the di-iodide[93], or palladium[94], or by decomposing $PdF_3.BrF_3$ in a vacuum at 200°.[92] It is a hygroscopic black powder, which evolves oxygen on contact with cold water, oxidises hydrogen chloride to chlorine, and reacts vigorously when heated with iodine, sulphur, phosphorus, carbon, sodium, magnesium, aluminium, or iron[88]. Complex fluorides of quadrivalent palladium A_2PdF_6 are known. The complexes are sensitive to moisture, decompose rapidly, and blacken in moist air[92,95].

A diminution in the stability of the higher valencies with increasing number of *d*-electrons is very characteristic of Group VIII in the Periodic System. This applies to all properties. Thus, in the iron family, iron trifluoride does not exhibit oxidising properties, cobalt trifluoride is an extremely strong oxidising agent, and nickel trifluoride (and tetrafluoride) have not been prepared, but from the properties of their complexes, appear to be extraordinarily strong oxidants. A similar increase in oxidising power from left to right is characteristic also of the higher fluorides of the platinum metals.

More than fifty years ago Ruff and his coworkers described the preparation, identification, and properties of three fluorides — OsF_4, OsF_6, and OsF_8 — of osmium[96]. But when the reaction of elementary fluorine with heated

osmium was reinvestigated, a single volatile reaction product was obtained, and was identified as osmium hexafluoride[97]. This compound is hydrolysed by aqueous alkali with the evolution of heat and a gas smelling like ozone, and it oxidises water to oxygen[24,97]. Osmium hexafluoride is reduced by a deficiency of iodine in iodine pentafluoride solution[98]. The reaction begins at room temperature, and terminates at 50° according to the equation

$$10OsF_6 + I_2 \rightarrow 10OsF_5 + 2IF_5.$$

The yield is quantitative. Osmium hexafluoride undergoes a similar transformation under the influence of ultraviolet radiation[98].

Golden-yellow iridium hexafluoride is obtained by the action of fluorine on iridium at 260°; it melts at 44.4° and boils at 53°.[99] Iridium hexafluoride is an extremely strong oxidising agent, reacting with hydrogen, sulphur, phosphorus, and halogens. It fluorinates even chlorine. It attacks glass even at room temperature, and fluorinates many metals, including platinum. Iridium hexafluoride oxidises water with the evolution of a gas smelling of ozone[24,99], and is reduced by carbon tetrachloride and by petroleum ether even in the cold. It is relatively stable in quartz, and does not decompose in the latter even at 400°.[99] The extraordinary reactivity of iridium hexafluoride is indicated also by its ability to fluorinate silver chloride. Polytetrafluoroethylene evolves carbon tetrafluoride on interaction with iridium hexafluoride[100].

In contrast to osmium, iridium forms complex fluorides of the type $AIrF_6$, which are strong oxidising agents. Hexafluoroiridates evolve oxygen on reaction with water, and are rapidly decomposed by moist air[99]. The extremely strong oxidant $IrOF_4$ is decomposed by water with the evolution of oxygen[99].

Platinum tetrafluoride decomposes with the evolution of fluorine when strongly heated[101]. The hexafluoride has recently been obtained[102,103] by the combustion of platinum in fluorine under the influence of an electric spark discharge; it is probably the strongest of all known fluorinating agents[24,26,103]. When stored in glass platinum hexafluoride, like neptunium and plutonium hexafluorides, undergoes photochemical decomposition[24]. It is unstable, undergoing rapid and complete decomposition at 280°.[24] It converts solid products of the radiolysis of neptunium and plutonium hexafluorides into the hexafluorides, although the yield is not high[24,103].

Platinum hexafluoride readily fluorinates bromine trifluoride to the pentafluoride at room temperature[103], reacts violently with metallic uranium to form the hexafluoride, and decomposes water with the evolution of oxygen[24]. The brownish-red platinum hexafluoride vapour oxidises molecular oxygen to a complex of the unusual type $O_2^+ PtF_6^-$.[104] Since the first ionisation potential of oxygen $O_2 \rightarrow O_2^+$ is 12.2 eV, which is higher than that of xenon (12.13 eV), it was suggested that formation of xenon hexafluoroplatinate

$$Xe + PtF_6 \rightarrow Xe^+PtF_6^-,$$

was possible. In fact, this method has been used to obtain the first chemical compound of xenon, which is orange in colour, is stable at 20°, and sublimes in a vacuum[86]. It is readily hydrolysed by water:

$$2XePtF_6 + 6H_2O \rightarrow 2Xe + O_2 + 2PtO_2 + 12HF.$$

8. Higher Fluorides of Copper, Silver, Gold, and Mercury

Copper forms a stable difluoride, which is devoid of oxidising power[105]. Copper trifluoride has not been described, although it may be involved as a fluorine carrier in the catalytic fluorination of organic compounds by elementary fluorine on copper gauze[106,107].

A complex K_3CuF_6 is formed[71] by the action of fluorine on a mixture of copper(II) and potassium chlorides at 250°. This substance is vigorously decomposed by water with the evolution of an unidentified gas (either O_2, O_3, or OF_2)[71]. Complexes A_3CuF_6 (A = Rb, Cs) are known[18]. Complexes of tervalent copper may be expected to exhibit interesting fluorinating properties.

Silver difluoride is one of the most thoroughly studied and widely used fluorinating agents. Treatment of silver or its salts with fluorine at 150–250° yields the black modification of the difluoride. The yellow modification can be obtained by fluorinating silver with chlorine trifluoride. The properties of silver difluoride have been studied in some detail[108].

Silver difluoride is widely used for the fluorination of organic compounds, being a more powerful fluorinating agent than is cobalt trifluoride[109]. It fluorinates carbon monoxide to carbonyl fluoride[110], and converts hydrocarbons and halogenated derivatives into perfluorohydrocarbons. Silver difluoride has the advantage over cobalt trifluoride in fluorinating chloro-derivatives, but, because of the poorer free-flowing properties of the powder and its more corrosive nature, it is inferior to the latter in the vapour-phase fluorination of hydrocarbons[111]. It has been reported that organic disulphides are selectively fluorinated by silver difluoride to derivatives of sulphur tetrafluoride, great prospects thus being opened up in the synthesis of organofluorine compounds. A special investigation has shown that silver difluoride is irreplaceable for this purpose[112]. This compound probably plays an extremely favourable role in the catalytic fluorination of organic compounds on a silvered wire[113].

Complex compounds based on the unknown silver trifluoride have been described[114-117]. Compounds of the type $AAgF_4$ (A = K, Cs) and $BaAgF_5$ react violently with water; at 200° $BaAgF_5$ is converted into the more stable compound $BaAgF_4$, fluorine being eliminated[117]. X-Ray examination has shown that compounds which had been regarded as $CsAgF_6$ and $CsAuF_6$ did not in fact have this structure[117].

Gold trifluoride has been obtained, by fluorinating gold with fluorine or with bromine trifluoride, as an orange powder, which decomposes at 500°. It is a strong fluorinating agent, reacting violently with water. It ignites organic compounds even at room temperature, and reacts smoothly with carbon tetrachloride at 40°.[114,118] Gold trifluoride probably has a favourable influence on the catalytic fluorination of organic compounds on a gold-plated copper wire[119].

A series of complex fluorides of the type $AAuF_4$ (A = Na, K, Cs, Ag) has been obtained by fluorinating the chloroaurates with elementary fluorine or by the reaction of gold trifluoride in bromine trifluoride with the metal fluorides. The complex $AgAuF_4$ does not react with carbon tetrachloride, but it is reduced by benzene, and reacts violently with cold water[114,118].

Mercuric fluoride has long been used as a reagent. It is a hygroscopic white substance of melting point 645°, which immediately becomes yellow in the air[120]. Its preparation has been described[120-122]. Mercury difluoride is used for the replacement of other halogens by fluorine, but at temperatures above 100° it mildly fluorinates hydrocarbons[120,123]. An interesting property is its ability to add on to fluorinated compounds containing multiple bonds (azomethines[124], alkenes[125,126]), so that it can be used for synthetic purposes according to the scheme[124]

$$CF_3N{=}CF_2 + HgF_2 \rightarrow (CF_3)_2NHgN(CF_3)_2 \xrightarrow{Br_2} (CF_3)_2NBr \xrightarrow{CF_2{=}CF_2} (CF_3)_2NCF_2CF_2Br.$$

III. HIGHER FLUORIDES OF ELEMENTS IN THE MAIN SUBGROUPS OF THE PERIODIC SYSTEM

In the following subgroups a high oxidising power is exhibited by the fluorides of tervalent thallium, quadrivalent lead, quinquevalent antimony and bismuth, oxygen, and sexivalent polonium, as well as all halogen fluorides. The fluorides of the inert gases which have recently been described must probably be included among fluorides of high oxidising power.

1. Higher Fluorides of Thallium, Lead, Antimony, and Bismuth

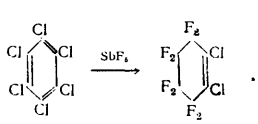
Thallium trifluoride can be obtained in several ways — by treating the oxide with fluorine at 300°,[127] or with bromine trifluoride[122] or sulphur tetrafluoride[121], by the action of chlorine trifluoride on metallic thallium[127], and by the interaction of thallium iodate with bromine trifluoride[122] — and is a white solid which darkens in moist air, being instantaneously hydrolysed by water with the formation of a black precipitate of the hydroxide

$$TlF_3 + 3H_2O \rightarrow Tl(OH)_3 + 3HF,$$

this giving the oxide Tl_2O_3 on being heated[122]. Thallium trifluoride does not react with liquid ammonia, but paraffin, benzene, and chloroform do interact with it, fluorination perhaps occurring here[127].

Lead tetrafluoride is obtained by fluorinating the difluoride with fluorine at 300°.[128] It consists of colourless crystals, which darken in the air owing to hydrolysis, and melt at around 600°.[128] Lead tetrafluoride vigorously fluorinates hydrocarbons in both liquid and vapour phases[129-131]. In practice, however, it is very difficult to use, since a eutectic mixture, containing about 60% PbF_2 + 40% PbF_4, attacks the reaction vessel[131]. The use has been reported of a mixture of lead dioxide, lead tetra-acetate, and anhydrous hydrogen fluoride[132] or of lead dioxide and sulphur tetrafluoride[133] in an autoclave, for adding fluorine at the double bond of halogenated alkenes.

Fluorides of tervalent and quinquevalent antimony are widely used in the exchange of other halogens for fluorine (the Swarts reaction)[134]. However, antimony pentafluoride is capable not only of exchanging chlorine for fluorine but also of adding fluorine to the double bond in chlorinated aromatic and unsaturated compounds[135,136]:



Antimony pentafluoride can be obtained from the pentachloride and anhydrous hydrogen fluoride or from the trifluoride and fluorine. It forms a hydrate $SbF_5.2H_2O$, as well as complexes which are stable in aqueous solution[137].

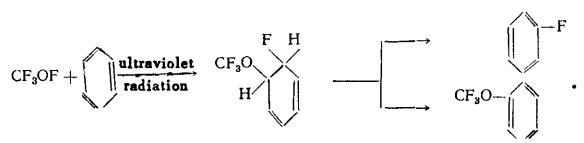
Bismuth pentafluoride is a stronger oxidising agent than is antimony pentafluoride. It reacts vigorously with water, a gas smelling of ozone being evolved[138,139], and reacts readily with paraffin oil, which is not blackened[139]. Its successful use for the synthesis of perfluorohydrocarbons has been reported[140]. However, the practical application of bismuth pentafluoride is made difficult by the complexity of its preparation, which involves passing fluorine over bismuth trifluoride at 450–500°. At this temperature the pentafluoride sublimes into the cooled part of the reaction vessel as long white needles, which instantly become yellow on contact with the air[138,139]. The yield of bismuth pentafluoride is low, obviously owing to its decomposition in the gaseous state[138]. Bismuth pentafluoride converts uranium tetrafluoride and oxide into uranium hexafluoride, and bromine into bromine trifluoride, which itself is converted into bromine pentafluoride[139].

The complex hexafluorobismuthates $ABiF_6$ are hygroscopic, and are decomposed even by 40% hydrofluoric acid[138]. Bismuth pentoxide reacts with the 40% acid with the evolution of a gas smelling of ozone. The resulting solution possesses extremely strong oxidising properties[138].

2. Fluorides of the Oxygen Subgroup

Oxygen forms with fluorine the difluoride OF_2 and several fluorides — O_2F_2, O_3F_2, and O_4F_2 — which are richer in oxygen[141]. Compounds of fluorine and oxygen with other elements are also known, such as trifluoromethyl hypofluorite CF_3OF,[141,142] fluorine nitrate NO_3F, fluorine perchlorate $ClFO_4$,[141] and compounds of the type XO_3F, where X = Cl, Br, I.[143] The oxygen fluorides are extremely strong oxidising agents even at low temperatures, and are employed in rocket technology[144-146]. Until recently oxygen difluoride has not been used for the synthesis of organofluorine compounds. When it interacts with benzene[147] and primary aliphatic amines[148], oxygen-containing products (quinones[147] and nitroso-compounds[148]) are isolated. Reaction with alkenes and alkynes yields α-fluoro-ketones, fluorohydrins, and $\alpha\alpha$-difluoro-ketones[149].

The readily available trifluoromethyl hypofluorite[141,142] adds quantitatively to the double bonds of alkenes[150-152]. It reacts slowly with benzene according to the equation[152]



Under the influence of ultraviolet radiation the hypofluorite reacts with methane[152]:

$$CF_3OF + CH_4 \xrightarrow[\text{radiation}]{\text{ultraviolet}} COF_2 + CH_3F + HF.$$

Among this group the most suitable for use for the preparation of organofluorine compounds is fluorine chlorate, which can be prepared by the action of fluorine on cooled potassium chlorate[153], by heating perchlorates or perchloric acid with excess of fluorosulphuric acid at a high temperature[154], or by treating them with a mixture of this acid and antimony pentafluoride at room temperature[155]. Fluorine

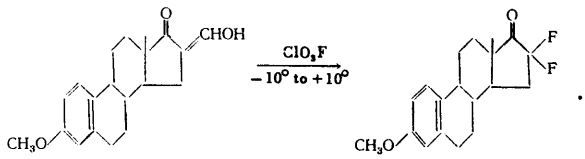
chlorate is a colourless substance melting at -110° and boiling at -46°.[153]. When heated it decomposes[156]:

$$2ClFO_3 = 2ClF + 3O_2.$$

Fluorine chlorate is able to replace the hydrogen atoms in reactive methylene groups[157,158], e.g. [157]

$$p\text{-}BrC_6H_4COCH_2COC_6H_4\text{—}Br\text{-}p \xrightarrow[\text{pyridine}]{ClO_3F,\ -10^\circ \text{ to } +10^\circ} p\text{-}BrC_6H_4COCF_2COC_6H_4\text{—}Br\text{-}p.$$

When this reagent is passed into an alcoholic solution of the sodium derivative of diethyl malonate, diethyl difluoromalonate is obtained[158]. Fluorine chlorate is employed for the fluorination of steroids[159-161], e.g. [161]



A method has recently been proposed for preparing *o*- and *p*-fluorophenols by treating the phenols with fluorine chlorate[162].

Sulphur tetrafluoride is used at the present time for replacing oxygen-containing groups by fluorine[163]. The hexafluoride is extremely stable[164]. The hexafluorides of selenium and tellurium do not exhibit oxidising properties[164].

It was earlier predicted that polonium would form a compound analogous to the Group VI hexafluorides SF_6, SeF_6, MoF_6, WF_6, and UF_6. However, no volatile compound was obtained when polonium-210 was heated in fluorine or when it was treated with liquid bromine trifluoride[26,165,166]. Treatment of polonium-208 with fluorine gave a volatile polonium fluoride, which underwent subsequent breakdown (chemical or radioactive). Perhaps its reactivity explains the lack of success of earlier attempts to prepare a volatile polonium compound[167].

3. Simple and Complex Halogen Fluorides

The halogen fluorides are extremely reactive substances, which can be arranged in the sequence of diminishing reactivity

$$F_2 > ClF_3 > BrF_5 > IF_7 > FCl > BrF_3 > IF_5 > BrF\ ^{168}.$$

Their reactions with many organic substances are very vigorous and may become explosive in character, so that the success of an experiment depends on the appropriate choice of technique.

Chlorine trifluoride, bromine trifluoride, and iodine pentafluoride are the most important as fluorinating agents, and possess several great advantages over both elementary fluorine and higher fluorides of metals. Firstly, they are liquid over quite a wide range of temperatures close to the normal, so that they can be more easily stored and used than can fluorine. Secondly, they do not leave any solid residues of the type of cobalt difluoride or silver fluoride after use, so that they are equally suitable for vapour-phase and for liquid-phase processes. Hitherto, however, the use of halogen fluorides has not been very widespread. The reasons are that they are too reactive and also that they usually introduce into the molecule not only fluorine but also, depending on the fluoride used, chlorine, bromine, or even iodine[169]. Sometimes this property is specially utilised; thus a mixture of halogens and halogen fluorides is an efficient source of halogen monofluorides in reactions with alkenes[170-172]:

$$IF_5 + 2I_2 = 5IF,$$

$$\overset{\delta+}{CF_2}=\overset{\delta-}{CF}\text{—}CF_3 + \overset{\delta+}{I}\ \overset{\delta-}{F} \rightarrow CF_3CFICF_3.$$

Iodine pentafluoride reacts with most organic compounds quite violently, sometimes even with ignition and evolution of hydrogen fluoride. However, insufficient study has been made either of the products or of the conditions of the reaction. Nevertheless, it is known that fluorobenzene is formed by reaction with benzene in the presence of the fluorides of arsenic and antimony[173].

The interaction of carbon tetrahalides with iodine pentafluoride has been described in detail[174], and the fluorination of carbon disulphide and carbonyl chloride with iodine pentafluoride has been studied[174]. Emeleus and Haszeldine obtained pentafluoroiodoethane from tetraiodoethylene and this pentafluoride[174].

Iodine heptafluoride is considerably more reactive than the pentafluoride. Although little work has been done on its reactions with organic substances, it is known to react with benzene in the presence of arsenic and antimony fluorides, yielding fluorobenzene[173].

Bromine trifluoride reacts explosively with the usual organic compounds. It can be successfully used for the partial replacement of other halogens by fluorine in polyhalogenated compounds, and for addition to multiple bonds in hexachlorobenzene, hexabromobenzene, and pentachlorotrifluoromethylbenzene[175,176]. However, this involves the addition to the double bonds not only of fluorine but also to some extent of bromine, obviously because the highly reactive bromine monofluoride is formed as an intermediate product. Bromine trifluoride can probably be used also for the fluorination of compounds containing some hydrogen; at least in the presence of boron trifluoride it replaces hydrogen in nitrobenzene by fluorine[173]. Selective fluorination of the nitrile group and the keto-group by bromine trifluoride in the presence of hydrogen fluoride or iodine pentafluoride at -15° has been reported[177,178]. Thus acetonitrile is converted into 1,1,1-trifluoroethane in yields of 70–90%. Under the same conditions acetone is converted into 2,2-difluoropropane in good yield (90%), but ketones of more complicated structure undergo cleavage.

Few data are available on the reactions of bromine pentafluoride. In the presence of phosphorus pentafluoride at low temperatures, for example, it converts bromobenzene into *p*-bromofluorobenzene[173].

Chlorine monofluoride is a very reactive gas, which sets fire to organic compounds. However, it can act on highly halogenated hydrocarbons, saturating double bonds and replacing hydrogen and part of the chlorine by fluorine[179].

Technical chlorine trifluoride is widely used in atomic and rocket technology[180]. In the absence of appropriate precautions, the interaction of this compound with the usual organic compounds is accompanied by explosion.

The reaction of benzene with chlorine trifluoride in polyfluorinated solvents[173] or carbon tetrachloride[181,182] in the presence of salts of various elements or of halogens as catalysts leads at low temperatures to the formation of fluoro- and chloro-benzenes[181,182], accompanied by low

yields of products involving addition of halogens to the ring carbon atoms[181,182]. Under the same conditions chlorobenzene gives *ortho*- and *para*-substitution products. Liquid-phase fluorination probably has an electrophilic mechanism[181,183]:

$$ClF_3+2CoF_2 \rightarrow 2CoF_3+ClF,$$
$$ClF_3+CoF_3 \rightarrow F^+ + CoF_4^- + ClF.$$

The vapour-phase halogenation of benzene with chlorine trifluoride, which is a free-radical process, yields a complex mixture of chlorofluorocyclohexanes[183,184]:

$$ClF_3 \rightarrow ClF+2F^{\cdot},$$
$$ClF \rightarrow Cl^{\cdot}+F^{\cdot},$$
$$C_6H_6 \xrightarrow{Cl^{\cdot},F^{\cdot}} C_6H_xCl_yF_z\ (x+y+z)=12.$$

Besides highly halogenated cyclohexanes, the mixture also contains chloro- and chlorofluoro-benzenes.

The liquid-phase halogenation of hexachlorobenzene with excess of chlorine trifluoride involves a chain of additions and vinyl and allyl substitutions leading to the formation of chlorofluorocyclohexenes $C_6F_nCl_{10-n}$ (n = 4–6). A very large excess (400%) yields chlorofluorocyclohexanes $C_6F_nCl_{12-n}$ (n = 5–7)[185].

Most of the information on the reactions of chlorine trifluoride with organic substances will be found in the patent literature, the investigations being aimed at obtaining greases and oils. Without going into details, we can summarise the results by stating that highly fluorinated chlorofluorohydrocarbons can be obtained by selecting appropriate conditions, but that, because of steric hindrance due to the massive chlorine atoms, replacement of the hydrogen is not complete[183,184], so that the products of the chlorofluorination are less stable, both thermally and chemically, than oils obtained in other ways.

A higher degree of replacement of hydrogen, and at the same time of chlorine, can be obtained in the presence of antimony salts, which obviously promote substitution of chlorine by fluorine, and thereby diminish the steric hindrance to replacement of the remaining hydrogen atoms[186]. More stable products are obtained by treating perchlorinated unsaturated and aromatic compounds[175,176,185,187].

The fluorination of carbon or coal, both by fluorine itself and by halogen fluorides, is of intrinsic interest. When fluorine, a mixture of fluorine and chlorine, or chlorine trifluoride is passed, diluted with nitrogen, through graphite or wood charcoal at temperatures between 160° and 660°, various perfluoro- or polychlorofluoro-carbons containing one or more carbon atoms are formed. Similar results are obtained with other halogen fluorides. The use of coal makes it possible to obtain products of far higher molecular weight and oils which distil between 100° at 1 atm and 250° at 20 mm.[188]

All halogen fluorides form complexes with metal fluorides. Such complexes can be obtained by two main methods — (1) direct mixing of the initial components[189,190], e.g.

$$AF + BrF_3 \rightarrow ABrF_4;$$

or (2) fluorination of metal halides with fluorine at high temperatures[191–195]

$$ABr \xrightarrow[t^\circ]{F_2} ABrF_4.$$

Complex halogen fluorides can also be prepared by treating iodates[122], chlorates[196], and metals (gold)[114] with bromine trifluoride. Iodine pentafluoride and the complex KIF_6 are obtained by the action of sulphur tetrafluoride on potassium iodate[197].

At the present time the following compounds are known

$$ACIF_4\ (A=K, Rb, Cs, Ag);\ RbClF_6,$$
$$ABrF_4\left(A=K, Rb, Cs, \frac{Ba}{2}\right);\ RbBrF_6;$$
$$AIF_4\ (A=K, Rb, Cs);\ AIF_6\ (A=Rb, Cs).$$

These complexes react violently with water, evolving oxygen, liberate iodine from potassium iodide solution[189,191,193,198], and oxidise nickel(II) salts to the quadrivalent state[191,193,198]. All the complexes obtained are milder halogenating agents than the corresponding halogen fluorides. The reactivity of the complex depends on the nature of the cation present in the outer sphere. Thus whereas under normal conditions $KBrF_4$ does not react with acetone, dioxan, or carbon tetrachloride, $AgBrF_4$ and $BaBr_2F_8$ ignite ether, acetone, petrol, and dioxan, but do not react with carbon tetrachloride. Bromine trifluoride not only ignites acetone and dioxan but also reacts violently with carbon tetrachloride[189]. The thermal stability of the complex halogen fluorides is increased by replacing the potassium cation by rubidium, and especially by caesium, while the violence of the reaction with water increases from iodine derivatives to those of bromine and chlorine[194].

The infrared spectra of the complex halogen fluorides have been recorded[194], their magnetic susceptibilities have been measured[194], and the structure of these interesting compounds has been discussed[199]. The fact that they exhibit a wide range of fluorinating activity makes them extremely promising materials for the synthesis of various organofluorine compounds.

In the electrochemical fluorination of salts of various amines it has been noted that bromide and iodide (but not chloride) anions have a favourable effect on the yield of perfluorinated products. The presence of iodine can be readily detected in fluorinated iodides from the characteristic colour, both in the electrolyte and in the perfluorinated raw material. The favourable effect of bromine and iodine may perhaps be explained by the mild fluorinating action of the complexes formed by organic bases with halogen fluorides.

4. Fluorine Compounds of the Inert Gases

As early as 1933 Pauling predicted the existence of KrF_6, XeF_6, and XeF_8. The first such compound, xenon hexafluoroplatinate, was obtained by oxidising xenon with platinum hexafluoride[86]. Four fluorides of xenon — XeF_2, XeF_4, XeF_6, and XeF_8 — have now been prepared[200,201].

Xenon difluoride is a colourless substance, which forms crystals reaching several millimetres in size. It melts at 140°, and can be supercooled to 50° without solidifying[201]. It is stable at room temperature, and can be stored in nickel or quartz vessels for several months. Xenon difluoride can be kept for a long time in sealed glass tubes at the temperature of solid carbon dioxide, but at room temperature it is slowly decomposed, even in the dark, by interacting with the glass. It reacts vigorously with methanol, and slowly with water. In solutions of alkalis and dilute acids it is decomposed, not especially violently, and it liberates iodine from acidified [potassium iodide] solution; it decomposes in dry paraffin[201], and dissolves in anhydrous hydrogen fluoride without decomposition. At

400° it is completely reduced by hydrogen to xenon and hydrogen fluoride[201].

Xenon tetrafluoride exists as colourless crystals melting at 114°.[201] It readily sublimes in a vacuum as large colourless crystals. Xenon tetrafluoride remains unchanged under vacuum in nickel or Pyrex glass for a month[200,201]. It attacks glass with the formation of silicon tetrafluoride and oxygen. Its mixtures with sugar or sulphur explode similarly to those with potassium chlorate. When deposited on paper or cotton wool, dry xenon tetrafluoride explodes on being heated; after it has become moist in the air, it instantly chars paper, and frequently it may even ignite spontaneously[201].

Xenon tetrafluoride fumes in the air, being hydrolysed to $Xe(OH)_4$, and dissolves in water, glacial acetic acid, and concentrated nitric and sulphuric acids; it reacts with acetic acid or acetic anhydride to give a crystalline substance, possibly xenon acetate. Cyclopentadiene, tetrahydrofuran, dioxan, and ethanol ignite under the influence of xenon tetrafluoride. Petrol dissolves it, and acetone reacts with it. Xenon tetrafluoride neither dissolves in nor reacts with carbon disulphide, carbon tetrachloride, dimethylformamide, diethyl ether, cyclohexane, and perfluoroheptane[201]. It oxidises metallic platinum to the tetrafluoride[201].

Xenon hexafluoride is a colourless crystalline substance of melting point 47.7° ± 0.2°;[201] it is stable at room temperature, and can be kept in a nickel vessel without decomposition for a week. Samples which have been sealed in quartz react slowly with the latter to give a colourless transparent liquid[202]. It dissolves in anhydrous hydrogen fluoride[202], the resulting solutions, unlike those of the difluoride and the tetrafluoride, possessing a high electrical conductivity, perhaps as a result of dissociation into the ions XeF_5^+ and HF_2^-. Hydrogen at room temperature and mercury at 100° reduce xenon hexafluoride to elementary xenon[201].

Xenon tetrafluoride and hexafluoride are hydrolysed according to the equations[203]

$$XeF_2 + H_2O \rightarrow Xe + 0.5\,O_2 + 2\,HF,$$
$$3XeF_4 + 6\,H_2O \rightarrow XeO_3 + 2Xe + 1.5\,O_2 + 12\,HF,$$
$$XeF_6 + 3\,H_2O \rightarrow XeO_3 + 6\,HF.$$

Alkaline hydrolysis of xenon hexafluoride yields xenic acid[201]. With boron trifluoride and arsenic pentafluoride at room temperature xenon hexafluoride forms addition products[201].

Xenon octafluoride has recently been synthesised in a sealed tube at room temperature. It is an unstable pale yellow gas which, when cooled in liquid nitrogen, is converted into a yellow solid[201,204].

The fluorides of xenon are of interest for the selective fluorination of alkenes, which can be effected in the vapour phase at room temperature. The xenon which is formed can be easily separated from the reaction product[205]. The reactivity of the fluorides increases with the proportion of fluorine in the molecule. Thus xenon hexafluoride, the most reactive of those studied, causes cleavage of the perfluoropropene molecule with the formation of hexafluoroethane and carbon tetrafluoride, whereas xenon difluoride does not react even after six days. The reaction with the tetrafluoride is represented by the equation

$$XeF_4 + 2\,CF_3CF{=}CF_2 \rightarrow 2\,CF_3CF_2CF_3 + Xe.$$

An interesting rearrangement takes place in the reaction of the xenon fluorides with aliphatic alkenes. Ethylene reacts with xenon difluoride and tetrafluoride at room temperature to form 1,1- and 1,2-difluoroethanes in 35% and 45% yield respectively. With propene, however, these fluorides give 1,1-difluoropropane as the main product (65%):

$$\left.\begin{matrix}XeF_2\\XeF_4\end{matrix}\right\} + \begin{matrix}CH_2{=}CH_2 \rightarrow CH_2FCH_2F + CH_3CHF_2 + Xe,\\CH_3CH{=}CH_2 \rightarrow CH_3CH_2CHF_2 + Xe.\end{matrix}$$

The relative instability of 1,2-difluoroethane and the enhanced stability of 1,1-difluoroethane suggest that the products formed initially isomerise under the reaction conditions into *gem*-difluorides. Furthermore, hydrogen fluoride is detected in the reaction mixture when the fluorides react with propene, which indicates partial fluorination of the methyl (allyl) group[205].

An unknown fluoride of radon RnF_x has been synthesised from the elements at 400°.[200,201] It is more stable and less volatile than xenon tetrafluoride. It is also reduced by hydrogen less vigorously than is the latter: at 200° the radon fluoride is stable in hydrogen, but at 500° and a hydrogen pressure of 800 mm it is completely reduced in 15 min.[200]

Krypton difluoride has now been obtained[206], by photochemical interaction of the elements mixed with argon[201] and by the action of a silent discharge on a mixture of the elements at low pressures (~20 mm) and temperatures (-183°)[206]. The difluoride is a crystalline substance which sublimes at temperatures considerably below 0°. It is kept in a dry Pyrex glass or polychlorotrifluoroethylene container at the temperature of solid carbon dioxide. It undergoes spontaneous decomposition at room temperature.

Hydrolysis of krypton difluoride is analogous to that of xenon difluoride[206]:

$$KrF_2 + H_2O \rightarrow Kr + 0.5\,O_2 + 2\,HF.$$

Hydrolysis is rapid also in acid solution, in contrast to xenon difluoride, which can exist in acid solution for a long time. Krypton difluoride reacts with antimony pentafluoride at -20° to form the compound $KrF_2.SbF_5$, this salt being more stable and less volatile than the difluoride itself. The complex is analogous to the salt $XeF_2.SbF_5$.[201,206]

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All fluorides of high oxidising power can be divided into five groups according to their oxidising activity. Assignment to one group or another is based on general chemical properties, and the boundaries between the groups are to some extent arbitrary.

I	II	III	IV	V
NiF_4, NiF_3 CoF_4 CuF_2 AgF_2 OsF_6 NdF_4 DyF_4 PdF_4	$ClF_3 > BrF_3 > IF_7 > ClF$ $PtF_6 > PuF_6$ RuF_6 NpF_6 BrF_5 RhF_6 IrF_6 $CrF_6 > MnF_4$ XeF_6 OsF_6	$AuF_5 > AgF_2 > CoF_3$ BiF_5 BrF_3 RuF_5 UF_6 $XeF_6 > XeF_4$ KrF_2	MnF_3 $PbF_4 > CeF_4$ PdF_3 RuF_4 RhF_4 IF_5 CrF_5 TlF_3 TbF_4 TcF_6 XeF_2 CF_3OF $FClO_3$	VF_5 SbF_5 HgF_2

The first group comprises higher fluorides which, because of their high reactivity and thermodynamic instability, have not yet been obtained in the free state, although they exist as complex derivatives. The second group includes fluorides possessing very high fluorinating power, being capable of fluorinating halides to halogen fluorides, and all other elements to higher fluorides; they ignite organic compounds even at room temperature. The third group contains fluorides which are capable of displacing chlorine from hydrochloric acid and oxygen (sometimes as ozone or oxygen difluoride) from water, and reacting with organic compounds to replace hydrogen by fluorine atoms; these fluorides may ignite on contact with some organic compounds at room temperature. The fourth group is represented by fluorides possessing moderate reactivity, although capable of replacing hydrogen by fluorine atoms. The fifth group comprises fluorides which, while being oxidising agents, are incapable of substituting fluorine for hydrogen in organic compounds, but are able in isolated cases to add fluorine to multiple bonds. In some cases the relative activities of the fluorides within the groups are known.

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OXIDATION OF ORGANIC COMPOUNDS WITH ACTIVE MANGANESE DIOXIDE

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I. INTRODUCTION

New oxidants, possessing a wide range of action and great selectivity, have been discovered in recent years, among them being nickel peroxide[1], manganese(III) acetate[2], osmium tetroxide, the chromium trioxide–pyridine complex[3], selenium dioxide[4], etc. An important place in this series is occupied by active manganese dioxide, which since 1948 has found wide application for the oxidation of various classes of substances, especially unstable natural