OXIDES AND OXYFLUORIDES OF THE HALOGENS

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Introduction

The existence of oxy-compounds of chlorine, bromine, and iodine has been known for a long time, and chlorine oxides, in particular, were the object of numerous investigations. These were limited, however, to physicochemical measurements, apart from work on hydrolysis or ammonolysis and on the respective oxidizing powers. Thus, especially in the 1920's and 1930's, the mechanism of formation and decomposition of these oxides became largely understood. Photochemical decomposition processes were

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also studied and a whole range of physical properties was determined. Subsequently, the structures of these compounds were determined by the use of electron diffraction and of infrared or Raman spectroscopy.

Only isolated studies of chemical reactions capable of being applied for preparative purposes were made. The reason for this may be that large-scale manipulation of the chlorine oxides is dangerous because of their explosive properties. Apart from dichlorine heptoxide, appreciable progress in the study of the chemical reactions of these oxides has been made only in the last ten years. Our knowledge of the oxides of bromine and iodine is still quite slight, and their polymeric character makes it difficult to make statements about definite compounds. Only a little is so far known about the chemistry of these oxides.

Directly related to the halogen oxides or anhydrides of the halogen oxyacids are the acid fluorides of the type XO_2F and XO_3F (where $X =$ chlorine, bromine, or iodine), some of which may be made directly by fluorinating the oxides. These compounds have been intensively studied in recent years and ClO_3F, in particular, has excited considerable interest. Compounds of the type XOF are not yet known. Interhalogens with the formula XF, which may be considered as fluorides of the acids XOH, will not be discussed here.

Finally, some reference may be made to the oxygen compounds of fluorine. They stand in a special relationship to the oxygen compounds of the remaining halogens since they should be considered rather as fluorides of oxygen. This stems from the fact that the electronegativity of fluorine is greater than that of oxygen and is implicit in the usual method of formulation as OF_2, O_2F_2, etc. The special position of the oxy-compounds of fluorine is also apparent from their completely different stoichiometry compared with the halogen oxides. This leads to the conclusion that, except in the case of OF_2, the structures and bonding are quite different. Nevertheless, a comprehensive description of these compounds seems desirable because of their contrast to the halogen oxides. It is also very topical because of the interest which the high oxidizing power of the oxygen compounds of fluorine has excited.

In this review new results on the chemistry of the halogen oxides, oxygen-fluorine compounds and halogen acid fluorides are presented. The results of older work are also discussed insofar as this seems necessary to characterize a compound as fully as possible with regard to its typical physical properties and, particularly, its chemical reactions. In those cases where several measurements or different results are available for certain physical properties, the more recent work is considered.

I. Oxygen-Fluorine Compounds

Only two oxygen compounds of fluorine, OF_2 and O_2F_2, were known until lately. Very recently A. V. Grosse proved the existence of O_3F_2 and thus confirmed the finding of Japanese workers which till then had been regarded with skepticism. Grosse succeeded finally in synthesizing the oxide O_4F_2. Practically nothing is known, however, about the chemical reactions of this class of compound.

A. Oxygen Difluoride OF_2

Oxygen difluoride was first obtained by Lebeau and Damiens (*106*) by electrolyzing KHF_2 in presence of water. Shortly afterwards they discovered a further preparative method based on the action of fluorine on aqueous caustic soda solution (*107*). These methods have remained unchanged in principle up to the present time. Finally, Engelbrecht and Nachbaur (*48*) studied the preparation of OF_2 and proposed the electrolysis of 80% aqueous hydrofluoric acid: this gives an anode gas containing 58% of OF_2, the remainder being oxygen.

The most important physical properties are shown in Table I. Vapor pressures between −195°C and −145°C may be represented by the equation $\log_{10} p_{\text{mm}} = 7.2242 - 555.42/T$ (*172*). The density of liquid OF_2 as a function of temperature is given by $d = 2.1315 - 0.00469\ T$ (*150*). Critical data are (*1*): $T_c = -58.0 \pm 0.1°\text{C}$; $V_c = 97.6\ \text{cm}^3/\text{mole}$; $p_c = 48.9$ atm.

Recent dipole moment measurements gave a value of $0.1759 \pm 0.0010\ D$; this has been interpreted as indicating a contribution of 2.1% of an ionic structure $O^{2+}(F^-)_2$ (*28*). [Note added in proof: Pierce *et al.* (*147a*) gave a value of $0.297 \pm 0.005D$ for the dipole moment.] Both the photochemical and the thermal decomposition of oxygen fluoride were investigated by Schumacher (*72, 99*). The thermal reaction occurs unimolecularly at 250°C to 280°C according to the equation

$$OF_2 \rightarrow F_2 + \tfrac{1}{2}O_2.$$

The theoretical prediction that a first order reaction should go over into one of second order at a certain pressure was first verified in the case of OF_2 by Schumacher (*177*).

Investigations on OF_2 reported so far are almost entirely physicochemical in character, and there are only isolated publications on its reactions. Exploratory studies of the action of OF_2 on solid inorganic compounds have demonstrated that its reactivity as a fluorinating agent is less than that of elementary fluorine (*150*). In aqueous solution it acts more as an oxidizing agent, in keeping with the strong affinity of fluorine for hydrogen (*86, 106, 150, 195*). Thus bromide and iodide are oxidized to bromine or iodine; prolonged reaction with aqueous alkalis yields oxygen:

$$OF_2 + 2OH^- \rightarrow 2F^- + H_2O + O_2.$$

B. Dioxygen Difluoride O_2F_2

Ruff and Menzel (*151, 152*) obtained O_2F_2 as an orange-red solid deposit on passing a stream of fluorine containing oxygen through a glow discharge,

TABLE I

PROPERTIES OF OXYGEN-FLUORINE COMPOUNDS

	OF_2	O_2F_2	O_3F_2	O_4F_2
M.p. (°C)	−223.8 (*152*)	−163.5 (*153*)	−189 (*98*)	Solid at −196; liquid at −183 (*78*)
B.p. (°C)	−145.3 (*172*)	−57.0 (*152*)		>−183 (*78*)
Decomposition temperature (°C)		>−57.0	>158 (*98*)	
Trouton's Constant	20.65 (*150*)	21.2 (*153*)		
Density (gm/ml at °C)	1.521 at −145.3 (*1*)	1.736 at −157.0 (*153*)	1.756 at −163 (*98*)	
Heat of formation (kcal mole^{-1})	−7.6 ± 2 (*53*)	+4.73 ± 0.30 (*97*)	+6.24 ± 0.75 (*97*)	
IR-Spectrum	(*91*) (*19*)	(*31*)		
Microwave spectrum		(*87*)		

the discharge tube being cooled in liquid air. The compound melts at −163.5°C to a cherry red liquid which decomposes rapidly to O_2 and F_2 in the neighborhood of its boiling point, −57°C. Thermal decomposition, which was measured between −60° and −25°C, is homogeneous and unimolecular (*69, 70*).

Vapor pressures measured below −100°C are represented by the equation $\log_{10} p_{\mathrm{mm}} = 7.515 - 1000/T$ (*153*). Liquid densities are given by $d = 2.074 - 0.00291\ T$ (*153*). The dipole moment is 1.40 D (*87*). For other physical properties see Table I.

Grosse succeeded recently in measuring directly the heat evolved in the decomposition of liquid O_2F_2 at −83°C into gaseous oxygen and fluorine, as well as that for the decomposition of liquid O_3F_2 at −152°C (*97*). From these values the heats of formation of gaseous O_2F_2 and O_3F_2 at 25° (see Table I) and the corresponding bond energies were calculated.

C. TRIOXYGEN DIFLUORIDE (OZONE FLUORIDE) O_3F_2

A compound with the composition O_3F_2 was first reported by Aoyama and Sakuraba (*2, 3*). Their discovery was not, however, generally accepted, possibly because an exact quantitative analysis was not given and because the possibility that oxygen was dissolved in O_2F_2 was not excluded. The existence of O_3F_2 as a definite compound was first confirmed by Kirshenbaum and Grosse in 1959 (*98*). An oxygen-fluorine mixture (3:2) was converted quantitatively into O_3F_2 in a glow discharge (2100–2400 volts; 25–30 ma) at a total pressure of 12 ± 1 mm and at liquid air temperature; the yield was 3–4 gm of O_3F_2 per hour.

In the meantime a further method of forming O_3F_2 was found, based on the decomposition of NF_3 with O_2 in a glow discharge (3700 volts; 20 ma; 0.6 torr) (*134*). A mixture of O_3F_2 and O_2F_2 condenses in the discharge tube, which is cooled with liquid nitrogen. Under these conditions NF_3 is clearly broken down completely since no compound containing the N—F bond can be condensed.

Properties (*98*). Ozone fluoride is a blood red viscous liquid, which remains liquid at −186°C and is thus readily distinguished from O_2F_2. The endothermic compound decomposes quantitatively and exothermally at about −158°C according to the equation

$$2O_3F_2 \rightarrow O_2 + 2O_2F_2.$$

It may be boiled under reflux in the temperature range −177° to −159°C at 0.1 to 1.5 torr with only a little decomposition, and it may also be distilled.

Vapor pressures, which were measured between −194° and −159°C, are represented by the equation: $\log_{10} p_{\mathrm{mm}} = 4.7277 - 520.7/T$. The liquid density is given by $d = 2.357 - 0.00676\ T$. Ozone fluoride is one of the strongest oxidizing agents known; like O_2F_2, it is appreciably more reactive than OF_2, F_2, or mixtures of O_2 and F_2, but by itself is not explosive. Organic compounds or other oxidizable materials inflame instantly or even explode.

At $-157°C$, O_3F_2 is readily soluble in $CFCl_3$ or CF_2Cl_2 over the whole concentration range. On the other hand it is insoluble at $-196°C$ in liquid fluorine, nitrogen or oxygen. Gaseous fluorine does not react with ozone fluoride at $-196°C$, but if the fluorine is activated by a discharge (3000–4000 volts; 30–60 ma), quantitative decomposition to O_2F_2 takes place:

$$2O_3F_2 + F_2^* \rightarrow 3O_2F_2.$$

D. TETRAOXYGEN DIFLUORIDE (OXAZONE FLUORIDE) O_4F_2

Grosse *et al.* (*78*) were able to isolate yet another oxygen fluoride, O_4F_2, which separated as a red-brown solid in a discharge tube at $-196°C$ using an O_2-F_2 total pressure of 5–15 torr and with a discharge operated at 840–1280 volts and 4.5–4.8 ma. The possibility of dissolved oxygen or ozone was excluded. At $-183°C$ O_4F_2 is a liquid with a vapor pressure less than 1 torr. Liquid O_4F_2 may be kept, at least for some hours, at $-183°C$. Slow decomposition to oxygen and ozone fluoride occurs between $-183°$ and $-163°$. Thus the following sequence of decomposition reactions for the oxygen fluorides may be set out:

$$O_4F_2 \xrightarrow{>-183°} \tfrac{1}{2}O_2 + O_3F_2$$
$$O_3F_2 \xrightarrow{-163°} \tfrac{1}{2}O_2 + O_2F_2$$
$$O_2F_2 \xrightarrow{-57°} O_2 + F_2.$$

E. THE STRUCTURE OF OXYGEN-FLUORINE COMPOUNDS

The structure of the angular molecule of OF_2 (symmetry C_{2v}) was elucidated through its infrared spectrum (*19*, *91*) and by the use of electron diffraction (*85*). The most probable values for the bond distance r_{O-F} is 1.418 Å, that for the valency angle being 103.2°. On the basis of the microwave spectrum Jackson (*87*) discussed a structure for O_2F_2 which was of the peroxide type. The following spread of possible values was given for the various parameters:

$$r_{F-O} = 1.44 - 1.54\ \text{Å};\ r_{O-O} = 1.28 - 1.48\ \text{Å};$$
$$\angle O{-}O{-}F = 109° - 110°;\ \text{dihedral angle} = 75\text{–}85°$$

Grosse concluded from a comparison of the estimated bond energy in O_2F_2 with that in other compounds that there was considerable resonance stabilization. Further discussions would be out of place in view of the very incomplete state of our knowledge of F_2O_2; this is even more true of O_3F_2 and O_4F_2.

II. Oxy-Compounds of Chlorine

Four oxides of chlorine have so far been isolated: in orders of increasing oxidation number of the halogen they are Cl_2O, ClO_2, Cl_2O_6, and Cl_2O_7. Their physical properties are given in Table II.

In addition the occurrence of ClO has also been established. This radical occurs both in the course of the decomposition of the chlorine oxides and also in reactions leading to their synthesis. The radical ClO has also been detected in an oxyhydrogen flame to which chlorine has been added. The radicals BrO and IO also occur in analogous conditions and indirect evidence for OF has been obtained in electron bombardment experiments. It has not, however, been possible so far to isolate ClO.

The existence of ClO_4, which was postulated by Gomberg, has not been confirmed. There was no indication of this compound either when Gomberg's experiments were repeated or in the course of the examination of a series of reactions of silver perchlorate with halogens in the most diverse organic solvents (*80*). It has, however, been discussed in relation to the decomposition of Cl_2O_7. According to Hüdepohl (*84*), the Gomberg reaction ($2AgClO_4 + I_2 \rightarrow 2AgI + 2ClO_4$) should be formulated as follows:

$$2AgClO_4 + I_2 \rightarrow AgI{\cdot}AgClO_4 + IClO_4.$$

A. DICHLORINE MONOXIDE Cl_2O

Dichlorine monoxide may, according to Bodenstein and Kistiakowski (*24*, *181*, *194*), be obtained as a brown solid by passing a mixture of chlorine and dry air in a ratio between 1:2 and 1:3 over HgO, and condensing the product in a vessel cooled in liquid air. The compound is extraordinarily unstable and may be exploded by shock or impact. It is also decomposed by light. The photochemical decomposition to chlorine and oxygen (*60*, *178*) proceeds by a primary cleavage into ClO and Cl.

$$\begin{aligned} Cl_2O + h\nu &\rightarrow ClO + Cl \\ Cl_2O + Cl &\rightarrow ClO + Cl_2 \\ ClO + ClO &\rightarrow Cl_2 + O_2. \end{aligned}$$

The chlorine-sensitized decomposition occurs similarly according to the following mechanism:

$$\begin{aligned} Cl_2 + h\nu &\rightarrow Cl + Cl \\ 2Cl_2O + 2Cl &\rightarrow 2ClO + 2Cl_2 \\ ClO + ClO &\rightarrow Cl_2 + O_2. \end{aligned}$$

TABLE II
PHYSICAL PROPERTIES OF THE OXIDES OF CHLORINE

Oxide/Property	Cl_2O	ClO_2	Cl_2O_6	Cl_2O_7
Molecular weight	87	67.5	167	183
M.p. (°C)	−116 (*75*)	−59 (*96*)	− +3.5 (*76*)	91.5 (*77, 209*)
B.p. (°C)	2.0 (*75*)	11.0 (*96*)	203 (calc.) (*76*)	80 (*77*)
Vapor pressure at 0°C	699 (*75*)	490 (*96*)	0.31 (*76*)	23.7 (*77*)
$\log p_{mm}$	$+7.87 - 1373/T$ (*75*)		$+7.1 - 2070/T$ Liquid $+9.3 - 2690/T$ Solid between −40°C and +20°C (*76*)	$+8.03 - 1818/T$ (*77*)
Trouton's constant	22.5 (*75*)	23.0 (*96*)	21 (*76*)	23.4 (*77*)
Heat of vaporization (kcal mole^{-1})	6.20 (*75*)	6.52 (*96*)	9.5 (*76*)	8.29 (*77*)
Heat of formation (kcal mole^{-1})	−18.26 (*207*) −18.1 ± 0.3 (*53*)	25.0 ± 1.5 (*53*)		
Density (gm cm^{-1} at °C)		1.64 at 0° (*33*)	2.02 at 3.5° (*54*)	1.86 at 0° (*125*)
Electron diffraction	(*43*)	(*43*)		
IR spectrum	(*82*)	(*82, 138, 188, 203*)		(*14, 188*)
Raman spectrum		(*102*)		(*61*)
Microwave spectrum	(*88*)	(*13*)		

Dichlorine monoxide is shown to be angular by its infrared spectrum (*82*), from electron diffraction studies (*32*, *43*, *142*) and from the microwave spectrum (*88*). The most probable value for the bond distance $r_{\mathrm{Cl-O}}$ is 1.701 Å, and for the valency angle $\angle$ClOCl is $110.8 \pm 1.0°$. The microwave spectrum shows that the molecule has substantial ionic character: a contribution of about 25% by the component $Cl^{+}OCl^{-}$ has been suggested.

Reactions of Cl_2O: Dichlorine monoxide is readily soluble in water and is partially decomposed to hypochlorous acid in an equilibrium reaction; hypochlorite is formed with aqueous alkali. The course of ammonolysis was formerly represented by the equation (*181*)

$$2Cl_2O + 10NH_3 \rightarrow 6NH_4Cl + 3H_2O + 2N_2,$$

but new studies (*101*) have shown that monochloramine and nitrogen chloride may also be isolated and are therefore very probably intermediates. In order to obtain evidence bearing on the course of the reaction, and particularly on the primary step in ammonolysis, the action of Cl_2O on alkyl amines was studied as a model reaction. Both mono- and di-alkylamines were converted into the corresponding chloramines (*101*).

$$Cl_2O + 2(C_2H_5)_2NH \rightarrow 2(C_2H_5)_2NCl + H_2O$$
$$Cl_2O + (C_2H_5)NH_2 \rightarrow (C_2H_5)NCl_2 + H_2O$$

Further investigations are needed, however, to show how far this observation is applicable to the ammonia reaction.

The reaction of dichlorine monoxide with the oxides of nitrogen, and especially with NO_2 and N_2O_5, has been studied in detail (*59*, *126*, *127*, *157*). In every case the product is chlorine nitrate, $ClNO_3$, which was first discovered by Martin and Jacobsen (*128*) in studying the system ClO_2-NO_2. The following set of reactions leading to the formation of $ClNO_3$ may be formulated on the basis of the kinetic studies of Martin and his co-workers (*126*), in which monofluorotrichloromethane, $CFCl_3$, and trifluorotrichloro ethane, $CF_2Cl{\cdot}CFCl_2$, were used as solvents:

$$Cl_2O + 2NO_2 \rightarrow ClNO_3 + NO_2Cl \qquad \text{(Gas, solution)}$$
$$2Cl_2O + 2NO_2 \rightarrow 2ClNO_3 + Cl_2 \qquad \text{(Melt)}$$
$$2Cl_2O + 2N_2O_5 \rightarrow 2ClNO_3 + 2NO_2Cl + O_2 \qquad \text{(Gas, solution)}$$
$$Cl_2O + N_2O_5 \rightarrow 2ClNO_3 \qquad \text{(Melt)}$$

It was found that Cl_2O does not react directly with N_2O_5 either in the gas phase or in solution, but reacts instead with the NO_2 produced in the decomposition of N_2O_5, and the latter process therefore controls the over-all reaction. The actual step leading to formation of chlorine nitrate in these reactions seems to be

$$ClO + NO_2 \rightarrow ClNO_3$$

in every case.

Simultaneously and independently Schmeisser and Fink (*59*, *157*) succeeded in carrying out the reaction between dichlorine monoxide and nitrogen pentoxide on a preparative scale. The larger quantities of chlorine nitrate which it was possible to make in this way allowed it to be used in the synthesis of inorganic acyl nitrates [e.g., $CrO_2Cl_2 + 2ClNO_3 \rightarrow CrO_2(NO_3)_2 + 2Cl_2$] and led to the first isolation of bromine nitrate and the iodine nitrates INO_3 and $I(NO_3)_3$ (*158*, *159*):

$$BrCl + ClNO_3 \rightarrow BrNO_3 + Cl_2$$
$$ICl + ClNO_3 \rightarrow INO_3 + Cl_2$$
$$ICl_3 + 3ClNO_3 \rightarrow I(NO_3)_3 + 3Cl_2$$

The reaction of nitric oxide and dinitrogen trioxide with Cl_2O at −78°C led mainly to N_2O_4 and chlorine (*101*). The occasional appearance of chlorine nitrate in the reaction makes it probable that it is also an intermediate in this case, since it can form dinitrogen tetroxide with nitric oxide ($ClNO_3 + NO \rightarrow NONO_3 + \frac{1}{2}Cl_2$) (*158*). It is impossible, however, to draw any firm conclusions above the course of the reaction from these purely preparative studies. The same is true of the interaction of dichlorine monoxide and nitrosyl chloride at −78°C, which yields chlorine, chlorine nitrate and N_2O_4 (*126*).

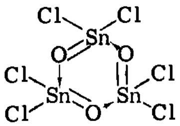
The reaction of Cl_2O with SO_3 was first investigated by Schützenberger (*174–176*). On passing Cl_2O over SO_3 he obtained a deep red liquid, which crystallized to bright red needles of m.p. 55°C. He ascribed the composition $Cl_2O{\cdot}4SO_3$ to this compound, which decomposed explosively if it was heated rapidly. A fresh study of this reaction (*201*), in which an SO_3 solution in $CFCl_3$ was added dropwise to a Cl_2O-$CFCl_3$ mixture at above −27°, also gave red crystals which melted at 56°C and were therefore identical with Schützenberger's product. This compound is not, however, a simple adduct but a chlorosyl-chloryl trisulfate, $(ClO)(ClO_2)(S_3O_{10})$, which is also produced by the interaction of SO_3 and ClO_2. When SO_3 reacts with Cl_2O it seems that ClO_2 is formed as an intermediate; the following mechanism was proposed for the reaction (*201*):

$$\begin{array}{l}
2Cl_2O \rightarrow 2ClO + 2Cl \\
2Cl_2O + 2ClO \rightarrow 2ClO_2 + 4Cl \\
2ClO_2 + 3SO_3 \rightarrow (ClO)(ClO_2)[S_3O_{10}] \\
\hline
4Cl_2O + 3SO_3 \rightarrow (ClO)(ClO_2)[S_3O_{10}] + 3Cl_2.
\end{array}$$

Recently Dehnicke discovered in the action of Cl_2O on metallic chlorides a method for the preparation of anhydrous oxychlorides (*39–41*). Dichlorine monoxide was passed as gas into the liquid chloride. These reactions take place very exothermally at room temperature without thermal decomposition of any significant part of the Cl_2O. Oxychlorides corresponding with the highest oxidation state always result because of the strong oxidizing action of Cl_2O and Cl_2.

Tin tetrachloride forms a white, amorphous and very hygroscopic oxychloride according to the equation

$$SnCl_4 + Cl_2O \longrightarrow SnOCl_2 + 2Cl_2$$



The oxychloride is high molecular in substance; according to molecular weight determinations it is trimeric. A ring-structure is proposed. It disproportionates at 155°C into tin dioxide and tin tetrachloride:

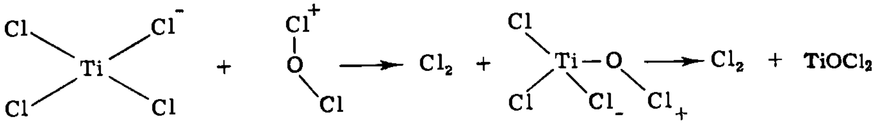
$$2SnOCl_2 \rightarrow SnO_2 + SnCl_4.$$

The pale yellow $TiOCl_2$ produced from $TiCl_4$ is crystalline. With $VOCl_3$, Cl_2O forms orange red crystalline VO_2Cl, which decomposes at 150°C into V_2O_5 and $VOCl_3$. Amorphous $PbOCl_2$ is violet:

$$TiCl_4 + Cl_2O \rightarrow TiOCl_2 + 2Cl_2$$
$$VOCl_3 + Cl_2O \rightarrow VO_2Cl + 2Cl_2$$
$$PbCl_4 + Cl_2O \xrightarrow{-10^\circ - 0^\circ} PbOCl_2 + 2Cl_2.$$

Tantalum pentachloride in carbon tetrachloride solution yields $TaOCl_3$ or $Ta_2O_3Cl_4$, according to the quantity of Cl_2O used. The oxychlorides give addition compounds with pyridine or $POCl_3$, except in the case of $PbOCl_2$.

There are indications that the reactions take place through the intermediate formation of hypochlorites. In the case of titanium tetrachloride, for example, the following reactions are possible:



The transformation of metal halides to oxychlorides can be applied directly to the corresponding bromides (liquid or molten). By the action of gaseous Cl_2O on tin or titanium tetrabromide the hitherto unknown oxybromides $SnOBr_2$ and $TiOBr_2$ are formed (*42*). These also give adducts with pyridine.

$$SnBr_4 + Cl_2O \rightarrow SnOBr_2 + Br_2 + Cl_2$$
$$TiBr_4 + Cl_2O \rightarrow TiOBr_2 + Br_2 + Cl_2.$$

Similar experiments with the halides of boron and aluminium were made by Schmeisser and Aubke (*169*), though these were directed not so much to the preparation of oxychlorides as to the preparation of anhydrous oxides at low temperatures. When boron trichloride or tribromide in solution in $CFCl_3$ at −30°C is decomposed with Cl_2O, flocculent B_2O_3 is precipitated and may be isolated by distilling off the solvent or filtration, and freed from halogen or excess of Cl_2O in vacuo at 70°C. The resulting hygroscopic B_2O_3 is found to be amorphous to X-rays. The same B_2O_3 is formed from undiluted BCl_3 and Cl_2O in the liquid state at −78°C. An analogous reaction occurs with Cl_2O and $AlBr_3$ at temperatures up to −20°C, though so far no halogen-free oxide has been obtained. Aluminium trichloride does not react with Cl_2O.

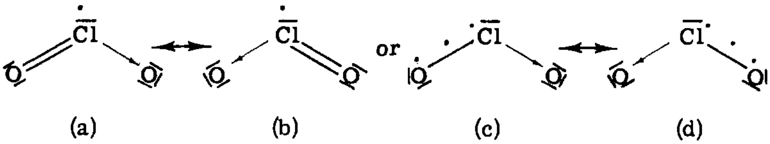
Attempts to fluorinate dichlorine monoxide have so far met with no success; elementary fluorine at −10°C and AgF_2 at room temperature failed to react (*59*, *122*) and no reaction was observed when OF_2 was led through liquid Cl_2O at −100°C (*170*).

B. Chlorine Dioxide ClO_2

1. *Preparation, Structure, and Properties*

The best laboratory method for preparing this compound is the action of sulfuric acid on potassium chlorate in the presence of a reducing agent, the most suitable being oxalic acid, since the ClO_2 is then diluted with CO_2 and manipulation becomes relatively free from danger. It is often advantageous to use solutions of chlorine dioxide in carbon tetrachloride; these are made by passing the mixture of ClO_2 and CO_2 coming from the generator into CCl_4 at 0°. Chlorine dioxide is yellow in the gaseous state, red brown as liquid and reddish yellow when solid. The most important physical properties are given in Table II.

Chlorine dioxide is paramagnetic because it has an odd number of electrons. The bond order calculated from the force constants is 1.5 (*188*); it has been deduced on theoretical grounds that the unpaired electron is not localized; ClO_2 therefore shows no tendency to dimerize. The electronic structure of ClO_2 may be described in valence-bond terminology by the following formulas, among others.



A very high dipole moment would be expected for a structure with three-electron bonds; it is estimated that it would be of the order of 3.4 *D* (*43*). It follows from the observed dipole moment of 0.78 *D* that structures (a) and (b) must be more important than (c) and (d) (*208*).

The bond distance r_{Cl-O} is calculated from the infrared spectrum as 1.49 Å, and the valency angle as 118.5° (*82*, *138*, *203*). The same distance has been found from new electron diffraction experiments, though the angle is given as 116.5° (*43*). From the microwave spectrum (*13*) the values $r_{Cl-O} = 1.47$ Å and $\angle OClO = 117.4°$ were obtained. The paramagnetic resonance spectrum has also been recorded (*18*).

Chlorine dioxide decomposes at higher temperatures or under the action of light; this is assumed to involve a chain reaction with the initial step

$$ClO_2 \xrightarrow[\Delta H]{h\nu \text{ or}} ClO + O$$

In addition to chlorine and oxygen, which are the end products, Cl_2O_6 is also formed by the steps (*25*, *179*)

$$ClO_2 + O \rightarrow ClO_3$$

$$ClO + O_2 \rightarrow ClO_3.$$

2. Reactions of Chlorine Dioxide

Hydrolysis with aqueous alkali yields chlorite and chlorate as the final products; ClO_2 is therefore usually considered as a mixed anhydride of the two acids. The kinetics of hydrolysis have recently been studied spectrophotometrically, conductometrically and by pH measurements (*20*). A first or second order reaction predominates, depending on the initial concentration; this is explained in terms of the equations below,

$$2ClO_2 + H_2O \rightarrow HCl_2O_5^- + H^+$$

$$ClO_2 + H_2O \rightarrow HClO_3^- + H^+$$

which show ClO_2 to react as a normal acid anhydride. However, secondary disproportionation occurs because of the instability of the acid formed. Chlorine dioxide does not react directly with water, though at low temperatures a solid hydrate is formed; this decomposes at +15°C (*191*). Reaction of ClO_2 with aqueous hydrogen peroxide according to the equation shown yields appreciable quantities of chlorous acid:

$$2ClO_2 + H_2O_2 \rightarrow 2HClO_2 + O_2$$

(Yields at 10°C between 26 and 39% $HClO_2$) (*37*).

Chlorine dioxide reacts with acceptors to form adducts (*160*). Antimony pentafluoride at −78°C in C_6F_{12} yields the white nonsublimable compound $ClO_2 \cdot SbF_5$, which melts at +83°C. In $CFCl_3$ as solvent at −10°C, ClO_2

and $SbCl_5$ give $ClO_2 \cdot SbCl_5$, which decomposes at about 80° with liberation of chlorine and formation of Sb_2O_5. With AsF_5 at −78° in $CFCl_3$, the compound $ClO_2 \cdot AsF_5$ results; it melts at 80° with decomposition. All these compounds react very violently with water or organic substances. Nothing is known so far about the bonding in these adducts; they may be considered as formally analogous to the nitrogen dioxide addition compounds $NO_2 \cdot AsF_5$, $NO_2 \cdot SbF_5$, and $NO_2 \cdot PF_5$. Elementary fluorine has no reaction on $ClO_2 \cdot AsF_5$ at +20°C (*59*), though the compound is converted to chloryl hexafluoroarsenate by chloryl fluoride (*199*):

$$ClO_2 \cdot AsF_5 + ClO_2F \rightarrow ClO_2[AsF_6] + ClO_2.$$

The reaction of ClO_2 with SO_3 was first examined by Lehmann (*108*). When ClO_2 was passed into liquid SO_3, products were isolated which contained chlorine, oxygen, and sulfur. The oxidation number of chlorine varied between 4 and 5 according to the quantity of ClO_2 used. It seems that mixtures of chlorosyl-chloryl-trisulfate, $(ClO)(ClO_2)S_3O_{10}$, and dichloryl trisulfate, $(ClO_2)_2S_3O_{10}$, must have been formed. Dichloryl trisulfate, m.p. 75.5°C, is obtained when a solution of SO_3 in $CFCl_3$ is added dropwise at −60° to a solution of ClO_2 in $CFCl_3$, so that ClO_2 is always in excess (*201*). The same compound results when ClO_2 is condensed into chlorosyl-chloryl-trisulfate and the mixture is allowed to warm in the course of 15 hours from −60° to 0°C (*201*). The reaction between SO_3 and excess of ClO_2 may thus be formulated in two stages:

$$2ClO_2 + 3SO_3 \rightarrow (ClO)(ClO_2)[S_3O_{10}]$$

$$(ClO)(ClO_2)[S_3O_{10}] + ClO_2 \rightarrow (ClO_2)_2[S_3O_{10}] + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}O_2$$

Dichloryl trisulfate may also be obtained from the reaction of SO_3 with $KClO_3$ or $KClO_2$ (*108*).

Formulation of the products as chlorosyl and chloryl compounds is in line with other work by Lehmann (*109*). When the adduct $N_2O_4 \cdot 4SO_3$ is heated a distillate of the composition $N_2O_4 \cdot 3SO_3$ results, which is considered to be $(NO)(NO_2)[S_3O_{10}]$. The chlorosyl or chloryl sulfates may be converted into the corresponding dinitrosyl or dinitryl compounds by the action of NO or NO_2 (see below under Reactions of Chloryl Compounds, Section II,C,*3*).

Chlorine nitrate was discovered by Martin and Jacobsen (*128*) in studying the system $NO_2/N_2O_4/ClO_2$ at 0°.

$$ClO_2 + 3NO_2 \rightarrow N_2O_5 + ClNO_3.$$

Reaction takes place via steps (1), (−1), (5), and (6) of the scheme given below. This reaction has also been investigated by Schmeisser and Fink (*59*, *157*). The action of ClO_2 with N_2O_5 may be represented approximately by the over-all equation (*128*):

$$4ClO_2 + 2N_2O_5 \rightarrow 4ClNO_3 + 3O_2.$$

Chlorine dioxide does not, of course, react directly with N_2O_5 but, as in the case of Cl_2O, with its decomposition products. The reaction scheme proposed for the reaction of ClO_2 with NO_2 or N_2O_5 is (*128*):

$$N_2O_5 \rightleftharpoons NO_3 + NO_2 \tag{1, -1}$$

$$NO_3 + NO_2 \rightarrow NO_2 + NO + O_2 \tag{2}$$

$$NO_3 + NO \rightarrow 2NO_2 \tag{3}$$

$$NO + ClO_2 \rightarrow NO_2 + ClO \tag{4}$$

$$NO_2 + ClO_2 \rightarrow NO_3 + ClO \tag{5}$$

$$NO_2 + ClO \rightarrow ClNO_3 \tag{6}$$

A summary of the reactions leading to formation of $ClNO_3$ from Cl_2O, ClO_2 and the nitrogen oxides NO_2 and N_2O_5 is given by Martin (*126*); further literature references are also given.

Reaction between ClO_2 and nitrosyl chloride takes place in the gas phase according to the equation

$$2NOCl + ClO_2 \rightarrow NO_2 + NO_2Cl + Cl_2.$$

Initially it is extraordinarily slow, but it may be induced by the addition of NO_2. The reaction is of zero order with respect to chlorine dioxide; its course is believed to involve a chain mechanism initiated by the process $NO_2 + ClO_2 \rightarrow NO_3 + ClO$ (*129, 130*).

Chlorine dioxide and chlorite, but not chlorates, are reduced to chloride by potassium borohydride (*21*).

$$8ClO_2 + 5KBH_4 \rightarrow 5KCl + 3HCl + 5H_3BO_3 + H_2O$$

The oxidation of phosphorus halides by ClO_2 in carbon tetrachloride solution has also been studied (*143*).

$$5PCl_3 + 2ClO_2 \rightarrow PCl_5 + 4POCl_3$$

$$3PI_3 + 3ClO_2 \rightarrow \tfrac{9}{2}I_2 + P_2O_5 + POCl_3$$

$$5PSCl_3 + 6ClO_2 \rightarrow 5SO_2 + 3PCl_5 + 2POCl_3.$$

Chlorine dioxide may readily be converted into chloryl fluoride, ClO_2F, by elementary fluorine or other fluorinating agents. These reactions are described in detail in the next section.

C. Chloryl Fluoride, ClO_2F

Chloryl fluoride was first obtained in 1942 by Schmitz and Schumacher (*171*), by fluorinating chlorine dioxide with elementary fluorine. This method is, however, troublesome because of the extraordinary violence of the reaction and, as a result, no further investigation on ClO_2F appeared for 10 years. In recent years the formation of ClO_2F has been studied by several workers. Three routes are available, namely fluorination of $KClO_3$, ClO_2, or Cl_2O_6 with elementary fluorine or other fluorinating agents.

1. *Preparation and Formation of ClO_2F*

a. Fluorination of $KClO_3$. The action of elementary fluorine on $KClO_3$ represents a method for the formation of chloryl fluoride rather than one for its preparation since it is formed only in small amounts and the main product is perchloryl fluoride (*22, 49, 50, 186*). These reactions are carried out between −40° and +30°C. Formation of ClO_2F is thought to arise from the combination of fluorine with ClO_2 produced by decomposition of the ClO_3^- anion, and is thus directly related to the formation from ClO_2 and fluorine. The course of the reaction when fluorine acts on potassium chlorate is discussed more fully when perchloryl fluoride is considered. Fluorination of $KClO_3$ may also be effected with other agents and the yields of ClO_2F are then better. Thus interaction with ClF_3 or BrF_3 leads almost exclusively to ClO_2F because of the higher reaction temperature needed (*50, 204*).

$$12KClO_3 + 20BrF_3 \rightarrow 12KBrF_4 + 4Br_2 + 6O_2 + 12ClO_2F.$$

Fluorsulfonic acid may also be used. It may be thought of as $HF{\cdot}SO_3$, the HF being the actual fluorinating agent, while SO_3 serves to combine with water liberated in the reaction. This method gives a 30% yield of ClO_2F based on the $KClO_3$ used, in addition to chlorine, chlorine dioxide and oxygen (*59*).

b. Fluorination of ClO_2. Chlorine dioxide combines directly with fluorine to form ClO_2F. As already mentioned, chloryl fluoride was first obtained in this way (*171*). When the reactants are brought together at room temperature only spontaneous decomposition of ClO_2 into chlorine and oxygen is observed. Formation of ClO_2F takes place only if the reactants are brought together at suitable partial pressures which are exactly maintained, or if, after condensing them together, they are warmed slowly from −78°C to +20°C. Reaction is homogeneous and bimolecular; at low ClO_2 concentrations and low pressures the rate controlling step is (*7*)

$$ClO_2 + F_2 \rightarrow ClO_2F + F.$$

This is followed by the wall reaction $2F \rightarrow F_2$. This reaction was developed later by Schumacher (*187*) into a preparative method. Large quantities of ClO_2F may be prepared by leading fluorine into liquid ClO_2 at −50°C.

Chloryl fluoride may also be prepared on a larger scale when fluorine is passed into solutions of ClO_2 in indifferent solvents; this eliminates the necessity for working with large quantities of condensed ClO_2. While in the case of carbon tetrachloride the relatively high crystallization temperature of the solvent limits the working temperature to a minimum of −20°C, at which only low concentrations are possible, it is feasible with $CFCl_3$ at −78°C to reach 3 millimole of ClO_2F per ml of solution. Such solutions are excellent for use in studying further reactions of chloryl fluoride (*45*, *161*). By cooling such solutions to −110°C, ClO_2F may be separated and obtained pure after distillation.

The simplest method for preparing chloryl fluoride is certainly to use AgF_2 as the fluorinating agent. When a slow stream of ClO_2 is passed at room temperature through a tube filled with argentic fluoride, quantitative reaction occurs and quite colorless chloryl fluoride may be condensed out in a trap cooled to −78°C (*160*).

$$AgF_2 + ClO_2 \rightarrow AgF + ClO_2F.$$

Consumption of argentic fluoride may readily be followed by observing the movement of the boundary between AgF_2 (brown) and AgF (yellow), and in this way excess of ClO_2 can be avoided. Cobalt trifluoride acts in the same way as AgF_2 (*160*). Chloryl fluoride is also produced when gaseous chlorine dioxide is passed through liquid BrF_3 at +30°C (*59*, *160*).

$$6ClO_2 + 2BrF_3 \rightarrow 6ClO_2F + Br_2.$$

c. Preparation of ClO_2F from Dichlorine Hexoxide. When dichlorine hexoxide is decomposed thermally in presence of fluorine between 22° and 48°C up to 75% of ClO_2F results (*4*, *5*). From the fact that no formation of ClO_3F can be detected, it may be concluded that neither Cl_2O_6 nor the ClO_3 radical derived from it is capable of reacting with fluorine. It is chlorine dioxide occurring in the decomposition process which unites with fluorine to give ClO_2F. A further product is Cl_2O_7, in amounts up to 25%. (For the formation of ClO_2F in the thermal decomposition of dichlorine heptoxide in presence of fluorine, see under Dichlorine Heptoxide, Section II,F).

Chloryl fluoride results quantitatively, in addition to nitryl perchlorate, from the action of nitryl fluoride on dichlorine hexoxide at 0°C (see under Dichlorine Hexoxide, Section II,D,*2*,*a*). It may also be made from dichlorine hexoxide using bromine trifluoride or pentafluoride as the fluorinating agent (*199*). Nothing definite can be said about the mechanism of the reaction, which occurs at −40°, at which temperature decomposition of the Cl_2O_6 to ClO_2 is excluded.

TABLE III

VAPOR PRESSURES OF CHLORYL FLUORIDE (*171*)

°C	−78	−65.5	−55	−45.5	−38	−30.2	−23.8	−17.2	−9.7	−6.3
mm of Hg	8.8	25.2	55.9	103.8	161.4	244	338	459	645	740

2. Reactions of Chloryl Fluoride: Formation of Chloryl Salts

Chloryl fluoride is thermally reasonably stable: decomposition at a measurable rate is first observed in a quartz vessel above 300°C. Glass is only slowly attacked at room temperature, though in presence of the least trace of water reaction is rapid; it is possible that dichlorine hexoxide is produced.

Chloryl fluoride is a true fluoride of chloric acid. Its hydrolysis, which has been investigated by several workers (*46*, *187*, *204*, *205*), follows essentially the course that would be expected.

$$ClO_2F + 2OH^- \rightarrow ClO_3^- + F^- + H_2O.$$

Even with careful work, however, the chlorate yields were a few per cent too low, and both chlorite and perchlorate were found to be present; this may be attributed to secondary decomposition of the chloric acid formed initially. Chlorine dioxide was detected as an intermediate product and, when the hydrolysis was effected with only a little water, dichlorine hexoxide was also observed. Decomposition of ClO_2F with ammonia occurs very vigorously, even at -78°C, but the only end products obtained were NH_4Cl and NH_4F (*59*).

Fluorides capable of forming complexes are converted to an extent depending on their complex forming powers into chloryl salts by the action of chloryl fluoride (*45*, *161*). The form of the vapor pressure curve of mixtures of SiF_4 and ClO_2F below -120°C suggests that an addition compound, probably $SiF_4 \cdot 2ClO_2F$, is formed. A compound isolated by Emeléus (*35*) by allowing ClO_2F to react with vanadium pentafluoride showed similar instability. While the product isolated at $-78°$ had the composition $VF_5 \cdot ClO_2F$, the composition at -46°C was $VF_5 \cdot 0{\cdot}63ClO_2F$. On the other hand a compound $ClO_2F \cdot BF_3$ or ClO_2BF_4, which could be sublimed at 0°C, was formed either by passing BF_3 into liquid chloryl fluoride or by its reaction with solutions of ClO_2F in $CFCl_3$. This compound also results directly by the union of chlorine dioxide and fluorine in the presence of BF_3; in this case yields are naturally very small since appreciable decomposition of chloryl fluoroborate occurs at room temperature. It is not possible to liberate chloryl fluoride from the compounds by means of NaF, as in the case of NOF from $NO(BF_4)$; the necessary reaction temperature cannot be attained because the chloryl compound is too volatile. The great volatility of this compound makes it unlikely that it is a true chloryl fluoroborate, and the formulation as an adduct is more likely. This is also in keeping with the observation that the compound attacks glass, just as ClO_2F itself does. This is probably also true in the case of the reaction product from phosphorus pentafluoride, $PF_5 \cdot ClO_2F$ or $ClO_2(PF_6)$.

Marked salt-like character is shown by the compounds $ClO_2(AsF_6)$

and $ClO_2(SbF_6)$, formed by stronger complexing fluorides. The increasing stability of the complexes as we pass to the hexafluoroantimonate is seen in the following table. The two complexes $ClO_2(BF_4)$ and $ClO_2(SbF_6)$ and

TABLE IV

COMPLEX COMPOUNDS OF ClO_2F WITH FLUORIDES

Compound	Reaction temperature (°C)	Temperature of incipient volatility (°C)	Decomposition temperature (°C)
$2ClO_2F \cdot SiF_4$	−150		> −120
$ClO_2F \cdot VF_5$	−78		> −78
$ClO_2[BF_4]$	−110	−78	+25
$ClO_2[PF_6]$	−78	−35	
$ClO_2[AsF_6]$	−78	+50	+150
$(ClO_2)_2[SnF_6]$	−70		> +160
$ClO_2[SbF_6]$	−10	m.p. +78	> +230

a compound of the composition $TaF_5 \cdot 0.48ClO_2F$ were also obtained by Woolf (*204*).

In the reaction of chloryl fluoride with AsF_3, its fluorinating action is apparent: the AsF_3 is transformed into AsF_5 or $ClO_2(AsF_6)$, and chlorine dioxide is also formed, according to the equation (*199*)

$$3ClO_2F + AsF_3 \rightarrow ClO_2(AsF_6) + 2ClO_2.$$

The fluorinating action of ClO_2F naturally shows itself in the reaction with chlorides. Metallic fluorides are first formed and, if these are capable of forming complexes, they then react with further ClO_2F to form chloryl salts (*59*, *160*). This method makes it possible to prepare chloryl salts from insoluble fluorides, such as SnF_4 and TiF_4. These are insoluble in liquid hydrogen fluoride and cannot therefore be induced to react with ClO_2F. Thus antimony pentachloride reacts with a large excess of chloryl fluoride according to the equation

$$6ClO_2F + SbCl_5 \rightarrow ClO_2(SbF_6) + 5ClO_2 + 2\tfrac{1}{2}Cl_2$$

Tin tetrachloride in $CFCl_3$ solution at −70°C gives dichloryl hexafluorostannate, which decomposes above 160° to SnO_2, SnF_4, ClO_2, and Cl_2.

$$6ClO_2F + SnCl_4 \rightarrow (ClO_2)_2(SnF_6) + 4ClO_2 + 2Cl_2.$$

Titanium tetrachloride reacts similarly, though reaction at −100°C is so vigorous, in spite of considerable dilution with $CFCl_3$, that pure $(ClO_2)_2TiF_6$ is not obtained. It is probably contaminated with TiF_4. Aluminium chloride is converted to AlF_3, which does not react further with ClO_2F.

Finally, chloryl fluoride is also able to fluorinate oxides. Corresponding experiments with SiO_2, Sb_2O_5, and B_2O_3 at −10°C showed the formation of SiF_4, $ClO_2(SbF_6)$ or $ClO_2(BF_4)$, in addition to ClO_2 and Cl_2O_6 resulting from decomposition of unstable chlorine oxides formed initially (*45*). Reaction of ClO_2F with iodine pentoxide follows a similar course; IF_5 and chlorine oxides are formed at −20°C (*199*).

Some investigations have been made on the reactions of chloryl fluoride with Lewis acids. Sulfur trioxide in $CFCl_3$ solution at −10° forms an orange colored chloryl salt of m.p. 27°C, which in the solid state must be $ClO_2^+SO_3F^-$ (*161, 204*)

$$ClO_2F + SO_3 \rightarrow ClO_2SO_3F$$

This substance may be considered as intermediate between the colorless chloryl salts, e.g., $ClO_2(SbF_6)$, and the deep red dichloryl trisulfate, $(ClO_2)_2[S_3O_{10}]$ (*108*).

Fluorsulfonic acid reacts with chloryl fluoride even at −78°C, and a red color is produced. The equilibrium

$$ClO_2F + HSO_3F \rightleftharpoons ClO_2SO_3F + HF$$

is established (*160*). Chloryl chlorosulfonate, on the other hand, is not stable; interaction of ClO_2F with chlorosulfonic acid at −78°C gives only the decomposition products ClO_2, chlorine, and SO_3 (*160*). Hydrogen chloride at −110°C yields HF, ClO_2, and chlorine (*160*):

$$ClO_2F + HCl \rightarrow HF + ClO_2 + \tfrac{1}{2}Cl_2.$$

The reaction with anhydrous perchloric acid, in which hydrogen fluoride and dichlorine hexoxide are produced, may be an equilibrium process (*45, 122, 162*) (see under Cl_2O_6, Section II,D,*2*,*a*). Finally mention may be made of the reaction with anhydrous nitric acid, in which nitryl perchlorate is obtained (*160*).

$$2ClO_2F + 2HNO_3 \rightarrow NO_2ClO_4 + ClO_2 + NO_2 + 2HF.$$

Presumably the unstable compound ClO_2NO_3 is formed initially and decomposes to NO_2 and ClO_3 or Cl_2O_6. The latter then react to form NO_2ClO_4. The last reaction may be shown to occur (*163, 199*). Secondary reactions between NO_2 and ClO_2 are discussed under chlorine dioxide.

It has not proved possible so far to prepare $ClO_2(BrF_4)$. There is no reaction between ClO_2F and BrF_3 either at −78°C or at +10°C. If, however, $ClO_2(SbF_6)$ is allowed to interact with BrF_3 the initial reaction occurs as follows (*160*):

$$ClO_2(SbF_6) + BrF_2(BrF_4) \rightarrow BrF_2(SbF_6) + ClO_2(BrF_4).$$

The compound $BrF_2(SbF_6)$ is known to be stable, whereas the chloryl compound decomposes at once as shown below.

$$ClO_2(BrF_4) \rightarrow ClO_2F + BrF_3.$$

This is in accord with observations on the interaction of $KClO_3$ with Sb_2O_5 and BrF_3, which also yields only chloryl fluoride (*205*).

$$12BrF_3 + 4KClO_3 + Sb_2O_5 \rightarrow 2BrF_2(SbF_6) + 4KBrF_4 + \tfrac{9}{2}O_2 + 3Br_2 + 4ClO_2F.$$

The well known chloryl sulfates which are formed either in the reaction of SO_3 with Cl_2O or ClO_2 or when sulfur oxychlorides or sulfur trioxide reacts with Cl_2O_6 are discussed in the sections dealing with the corresponding chlorine oxides.

3. Reactions of Chloryl Compounds

The chloryl component may be displaced from compounds by means of nitrogen oxides; nitryl or nitrosyl compounds result and the chlorine oxide is set free. Thus nitrogen dioxide reacts with chloryl hexafluoroarsenate according to the equation (*160*):

$$ClO_2(AsF_6) + NO_2 \rightarrow NO_2(AsF_6) + ClO_2.$$

Chlorine nitrate is also formed by secondary reactions between NO_2 and ClO_2 both in this case and in some of the reactions described subsequently. Decomposition with NO follows an analogous course (*160*):

$$ClO_2(AsF_6) + NO \rightarrow NO(AsF_6) + ClO_2.$$

In this case however a redox reaction between ClO_2 and NO gives NO_2 as a secondary product. This also participates in the reaction so that $NO(AsF_6)$ may be isolated only as a mixture with $NO_2(AsF_6)$. Decomposition of $ClO_2(AsF_6)$ with nitryl chloride at −30°C also leads to $NO_2(AsF_6)$ (*59*)

$$ClO_2(AsF_6) + NO_2Cl \rightarrow NO_2(AsF_6) + ClO_2 + \tfrac{1}{2}Cl_2.$$

The following reactions are also of the type discussed above:

$$(ClO)(ClO_2)S_3O_{10} + 2NO \xrightarrow{-160^\circ} (NO)_2S_3O_{10} + [Cl_2O_3]\ (\mathit{201})$$

$$(ClO)(ClO_2)S_3O_{10} + 2NO_2 \xrightarrow{+5^\circ} (NO_2)_2S_3O_{10} + [Cl_2O_3]\ (\mathit{59}).$$

In the case of the reaction with NO large quantities of N_2O_3 are also formed.

The reactions of "chloryl perchlorate," ClO_2ClO_4 (= Cl_2O_6), are described under dichlorine hexoxide.

D. DICHLORINE HEXOXIDE Cl_2O_6

1. *Formation and Preparation*

The formation of Cl_2O_6 in the photochemical reaction of chlorine with ozone was studied by Bodenstein and his co-workers (*25, 26*). Red light, which is absorbed by O_3, leads to the formation of Cl_2O_6, whereas light which is absorbed by chlorine only produces decomposition of the ozone. In the thermal reaction of chlorine with ozone the intermediate formation of ClO, ClO_2, ClO_3, and ClO_4 has been postulated (*5, 27*). The mechanism has been discussed recently by Szabo (*193*), who formulated the reaction leading to dichlorine hexoxide in terms of the equilibrium

$$ClO + O_2 \rightleftharpoons ClO_3 \rightleftharpoons \tfrac{1}{2}Cl_2O_6.$$

The reaction $ClO + O_2 \rightarrow ClO_3$ is thermoneutral (*73*). Since ClO is always produced as an intermediate in the decomposition reactions (*193*)

$$Cl + Cl_2O \rightarrow ClO + Cl_2 + 14\ \text{kcal}$$
$$ClO_2 + O \rightarrow ClO + O_2 + 48\ \text{kcal}$$

it is evident that this species occupies a key position in reactions involving both the formation and decomposition of chlorine-oxygen compounds.

Kinetic studies also led to a convenient preparation method from chlorine dioxide and ozone, since Schumacher and Stieger (*180*) came to the conclusion in discussing their results that the reaction

$$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$$

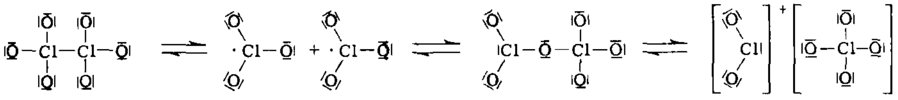
must take place with only a small activation energy. They succeeded in carrying out the reaction on a preparative scale and this method is still used exclusively in the laboratory.

Whereas virtually only ClO_3 is present in the gas phase (*74*) the liquid oxide consists mainly of the dimer, though the presence of monomer may be detected by magnetic measurements (*54*). The dissociation energy for the reaction $Cl_2O_6 \rightarrow 2ClO_3$ is only 1.5 kcal.

2. *Reactions of Cl_2O_6*

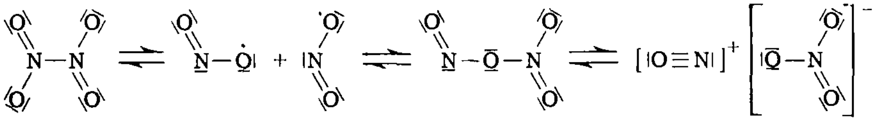
a. Cl_2O_6 Considered as Chloryl Perchlorate. In an extensive experimental study by Schmeisser and his co-workers (*162*) it was found that Cl_2O_6 is able to react as if it were chloryl perchlorate, $ClO_2^+ClO_4^-$, as Lehmann (*108*) also supposed. The first proof of this came from the reaction $ClO_2F + HClO_4 = HF + ClO_2ClO_4$ (see below in this subsection).

Dichlorine hexoxide is not able to go over directly into this polarized from. It is necessary to assume cleavage, followed by rearrangement:



$Cl_2O_6 \rightleftharpoons 2ClO_3 \rightleftharpoons O_2ClOClO_3 \rightleftharpoons ClO_2^+ClO_4^-$ (= Chloryl perchlorate).

This scheme for the reactive forms of Cl_2O_6 is completely analogous to those discussed for N_2O_4 (*185*)



$N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons ONONO_2 \rightleftharpoons NO^+NO_3^-$ (= Nitrosyl nitrate).

Both NO and NO_2 react with Cl_2O_6 (in carbon tetrachloride solution) at 0°C with displacement of the "chloryl cation" and formation of the corresponding perchlorates, chlorine dioxide being set free. As would be expected N_2O_3 reacts as a mixture of NO and NO_2 (*163*, *199*).

$$NO + ClO_2^+ClO_4^- \rightarrow NO^+ClO_4^- + ClO_2$$
$$NO_2 + ClO_2^+ClO_4^- \rightarrow NO_2^+ClO_4^- + ClO_2$$
$$N_2O_3 + 2ClO_2^+ClO_4^- \rightarrow NO^+ClO_4^- + NO_2^+ClO_4^- + 2ClO_2$$

Possible secondary reactions of the nitrogen oxides with ClO_2 leading to $ClNO_3$ have already been described in connection with the reactions of chlorine dioxide.

The reaction with N_2O_5 (= NO_2NO_3) is not quite so straightforward. Nitryl perchlorate is probably formed initially but chloryl nitrate, (ClO_2NO_3), which, at least formally, must be the other product, decomposes at once. This gives rise to secondary reactions in which chlorine nitrate and oxygen are produced (*199*).

$$2NO_2^+NO_3^- + 2ClO_2^+ClO_4^- \rightarrow 3NO_2^+ClO_4^- + ClNO_3 + \tfrac{1}{2}O_2.$$

In addition there is a reaction between Cl_2O_6 and chlorine nitrate, the course of which has been elucidated in separate experiments (*199*).

$$ClNO_3 + ClO_2^+ClO_4^- \rightarrow NO_2^+ClO_4^- + ClO_2 + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}O_2.$$

The over-all reaction between N_2O_5 and Cl_2O_6 may then be represented by the equation:

$$2NO_2^+NO_3^- + 3ClO_2^+ClO_4^- \rightarrow 4NO_2^+ClO_4^- + ClO_2 + \tfrac{1}{2}Cl_2 + O_2.$$

The interpretation of the course of the reaction is supported not only by the well-defined end products mentioned but also by the fact that small amounts of $ClNO_3$ could be isolated. The chlorides of the nitrogen oxyacids react similarly with Cl_2O_6 in CCl_4 as solvent at −20°C (*123*, *162*).

$$NO^+Cl^- + ClO_2^+ClO_4^- \rightarrow NO^+ClO_4^- + ClO_2 + \frac{1}{2}Cl_2$$
$$NO_2^+Cl^- + ClO_2^+ClO_4^- \rightarrow NO_2^+ClO_4^- + ClO_2 + \frac{1}{2}Cl_2.$$

When NO_2F is passed into a solution of Cl_2O_6 in $CFCl_3$ at 0° a smooth formation of ClO_2F and nitryl perchlorate is observed

$$NO_2^+F^- + ClO_2^+ClO_4^- \rightarrow NO_2^+ClO_4^- + ClO_2F.$$

The reaction products are unable to interact in the reverse direction (*160*).

In the double decomposition of Cl_2O_6 with anhydrous hydrogen fluoride in a platinum apparatus at 6°C an equilibrium is set up in which chloryl fluoride and perchloric acid are produced (*45, 122, 162*).

$$Cl_2O_6 + HF \rightleftharpoons HClO_4 + ClO_2F.$$

The fact that Cl_2O_6 behaves as chloryl perchlorate is shown not only by the reactions described, but also by experiments in which perchlorates are actually prepared with the help of Cl_2O_6. These have led to the discovery of a new type of inorganic acyl perchlorate.

Acyl chlorides undergo a general reaction with dichlorine hexoxide in which they are transformed to acyl perchlorates (*123, 162*). Chromyl chloride reacts with excess of Cl_2O_6 at the melting point of the latter (+3.5°C) to form the red liquid chromyl perchlorate $CrO_2(ClO_4)_2$, which can be distilled in high vacuum at 35°C.

$$CrO_2Cl_2 + 2Cl_2O_6 \rightarrow CrO_2(ClO_4)_2 + 2ClO_2 + Cl_2.$$

Chromium trioxide is formed as a by-product and is, indeed, the only product containing chromium if CrO_2Cl_2 is used in excess. Chromyl perchlorate reacts with CrO_2Cl_2 to form Cr_3O_8 or CrO_3, chlorine dioxide, chlorine, and oxygen.

$$3CrO_2(ClO_4)_2 + 3CrO_2Cl_2 \rightarrow 2Cr_3O_8 + 6ClO_2 + 3Cl_2 + 4O_2.$$

Both this reaction and the formation of CrO_3 in the interaction of CrO_2Cl_2 with Cl_2O_6, make it likely that the latter reaction takes place via CrO_3 as an intermediate:

$$CrO_2Cl_2 + Cl_2O_6 \rightarrow CrO_3 + 2ClO_2 + Cl_2 + \frac{1}{2}O_2$$
$$CrO_3 + 2Cl_2O_6 \rightarrow CrO_2(ClO_4)_2 + 2ClO_2 + \frac{1}{2}O_2.$$

Chromyl perchlorate may also be made by the direct action of Cl_2O_6 on CrO_3.

Vanadium oxytriperchlorate may be obtained by treating V_2O_5 with a large excess of Cl_2O_6 at 5°C.

$$2V_2O_5 + 12Cl_2O_6 \rightarrow 4VO(ClO_4)_3 + 12ClO_2 + 3O_2.$$

The compound $VO(ClO_4)_3$, which crystallizes at 21–22°C, may be distilled in high vacuum at 33.5°C. It reacts extremely violently with $VOCl_3$. Even at temperatures only a little above −180°C sudden formation of ClO_2, chlorine and oxygen occurs and VO_2ClO_4 remains:

$$2VO(ClO_4)_3 + VOCl_3 \rightarrow 3VO_2(ClO_4) + 3ClO_2 + \tfrac{3}{2}Cl_2 + \tfrac{3}{2}O_2.$$

The same compound results from $VOCl_3$ and Cl_2O_6 at 5°C in CCl_4 as diluent; undiluted $VOCl_3$ reacts explosively with Cl_2O_6.

$$VOCl_3 + 2Cl_2O_6 \rightarrow VO_2ClO_4 + 3ClO_2 + \tfrac{3}{2}O_2.$$

Reaction of Cl_2O_6 with an excess of tin tetrachloride occurs at the melting point of the latter (−33°C) to give a mixture of solids, melting at 40–50°C and becoming red. In high vacuum at 50° it is possible to distil red $SnCl_2(ClO_4)_2$ from the melt. It crystallizes slowly at room temperature and decomposes to tin oxychloride in CCl_4 solution.

$$SnCl_2(ClO_4)_2 \rightarrow SnOCl_2 + [Cl_2O_7].$$

With the reverse proportions of Cl_2O_6 and $SnCl_4$ very hygroscopic red crystals of the composition $Sn(ClO_4)_4{\cdot}2Cl_2O_6$ are formed at −30°C.

$$SnCl_4 + 6Cl_2O_6 \rightarrow Sn(ClO_4)_4{\cdot}2Cl_2O_6 + 4ClO_2 + 2Cl_2.$$

These react with chlorine nitrate (*59*) and with NO_2 (*123*) forming nitryl perchlorate and tin tetranitrate respectively.

In the reaction of Cl_2O_6 with silicon tetrachloride at room temperature products are formed with a lower perchlorate content than that required for $Si(ClO_4)_4$. The latter may possibly be formed as the primary product, but it loses Cl_2O_7 and forms Si—O—Si bonds, i.e., tends to form SiO_2 as the end product.

In carbon tetrachloride at −25°C thionyl chloride reacts with Cl_2O_6, via a primary oxidation of $SOCl_2$ to SO_3, to give dichloryl trisulfate, which may also be made directly from SO_3 and Cl_2O_6 (*108*).

$$\begin{array}{c}
3SOCl_2 + 3Cl_2O_6 \rightarrow 3SO_3 + 6ClO_2 + 3Cl_2 \\
3SO_3 + 2Cl_2O_6 \rightarrow (ClO_2)_2S_3O_{10} + [Cl_2O_7] \\
\hline
2SOCl_2 + 5Cl_2O_6 \rightarrow (ClO_2)_2S_3O_{10} + 6ClO_2 + 3Cl_2 + [Cl_2O_7]
\end{array}$$

Reaction of SCl_2 with Cl_2O_6 gives the same end products, but SO_2Cl_2 does not react with Cl_2O_6.

b. Other Reactions of Cl_2O_6. The oxidizing action of dichlorine hexoxide is apparent in the reaction with iodine or the iodine chlorides ICl and ICl_3: in each case mixtures of I_2O_5 and ICl_3 result (*200*).

The ClO_3 radical, which is present in liquid Cl_2O_6, may be trapped with AsF_5. At −10°C an adduct with the formula $ClO_3{\cdot}AsF_5$ is obtained. It is impossible to avoid contamination with $ClO_2{\cdot}AsF_5$ (ClO_2 being a decomposition product of Cl_2O_6), but the melting point of the product (118°C) differs significantly from that of $ClO_2{\cdot}AsF_6$ (78°C). The product cannot be sublimed and reacts explosively with water (*199*). At −50° it reacts with chloryl fluoride according to the equation (*199*):

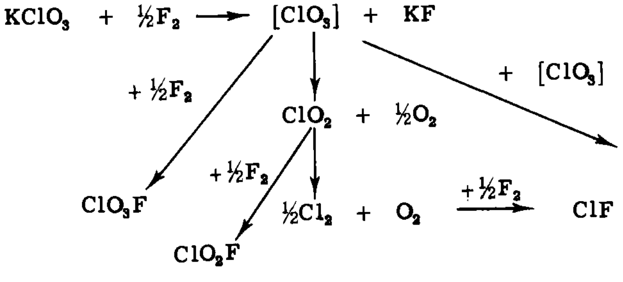
$$2ClO_2F + 2ClO_3{\cdot}AsF_6 \rightarrow 2ClO_2(AsF_6) + Cl_2O_6.$$

Unlike chlorine dioxide, dichlorine hexoxide is unable to react directly with fluorine. Between 20° and 40°C in the thermal decomposition of the hexoxide in presence of fluorine only ClO_2F, and no ClO_3F, is obtained. The fact that Cl_2O_7 is also formed makes it clear that fluorine reacts only with the decomposition products of Cl_2O_6. Fluorination of Cl_2O_6 is, however, possible with bromine trifluoride; while chloryl fluoride is produced with this reagent (see under chloryl fluoride, Section II,C,*1*,*b*), BrF_5 gives ClO_2F and BrO_2F (see below under bromyl fluoride, Section III,D,*1*).

E. Perchloryl Fluoride, ClO_3F

1. Formation, Preparation and Structure of ClO_3F

a. From Potassium Chlorate and Fluorine. Perchloryl fluoride was first detected in 1951 by Bode and Klesper as a product of the action of elementary fluorine on potassium chlorate at −40°C (*22*, *23*). These experiments were repeated by Engelbrecht (*49*, *50*). Yields of ClO_3F were about 45%, based on the fluorine used. In this somewhat obscure decomposition ClO_2F, ClF, Cl_2, Cl_2O_6, and O_2 are also formed. Engelbrecht discussed the following reaction scheme (*50*)



A little later the reaction was reinvestigated by Schumacher (*186*). Working below −20°C he was able under certain conditions to obtain ClO_3F in yields of 60%; the by-products were Cl_2, OF_2, and ClO_2F and its decomposition products.

b. Electrolysis of Sodium Perchlorate in Anhydrous Hydrogen Fluoride. Electrochemical fluorination of a 10% solution of $NaClO_4$ in anhydrous hydrogen fluoride at 0°C and 4–7 volts, using nickel anodes, likewise leads to formation of ClO_3F (*50, 164*). This electrolytic method has only a limited value since the yields are not particularly high and chlorine oxides and hydrogen are produced, in addition to OF_2, Cl_2, or O_2, and this can lead to explosions (*164*).

c. From Sodium Perchlorate and Fluorsulfonic Acid. When sodium perchlorate is warmed to 60–70°C with excess of fluorsulfonic acid, ClO_3F is formed in yields up to 73%. After washing with alkali thiosulfate solution and drying with concentrated sulfuric acid it is completely pure. This process was discovered simultaneously and independently by several workers (*15, 103, 104*) and is applicable on the kilogram scale.

On the basis of Fredenhagen's investigations (*62–64*), which showed that perchloric acid acts as an ampholyte in liquid hydrogen fluoride and that in dilute solutions of $KClO_4$ in liquid hydrogen fluoride the equilibrium

$$KClO_4 + 2HF \rightleftharpoons K^+ + 2F^- + (H_2ClO_4)^+.$$

predominates, Lang (*104*) proposed the following reaction scheme. In it, fluorsulfonic acid act simultaneously as a fluorinating and a dehydrating agent:

$$\begin{array}{c}
NaClO_4 + HSO_3F \rightleftharpoons Na^+ + HClO_4 + SO_3 + F^- \\
HSO_3F \rightleftharpoons H^+ + SO_3 + F^- \\
HClO_4 + H^+ \rightleftharpoons (H_2ClO_4)^+ \\
(H_2ClO_4)^+ + SO_3 + F^- \rightarrow ClO_3F + H_2SO_4 \\
H_2SO_4 + SO_3 \rightarrow H_2S_2O_7 \\
\hline
NaClO_4 + 2HSO_3F \rightarrow ClO_3F + H_2S_2O_7 + Na^+ + F^-.
\end{array}$$

Alternatively the course of the reaction has been discussed in terms of the perchloryl ion (*16, 206*):

$$2HSO_3F + HClO_4 \rightleftharpoons ClO_3^+ + 2SO_3F^- + H_3O^+.$$

In addition to sodium perchlorate it is possible to use alkali and alkaline earth perchlorates in general and also perchloric acid. Perchloryl fluoride may also be prepared from perchlorates and antimony pentafluoride in place of fluorsulfonic acid. It is advantageous to use a mixture of the two with 60–70 wt% of SbF_5 and a reaction temperature between 70° and 130°C; yields up to 97% are attained (*17, 51*).

d. From Dichlorine Heptoxide and Fluorine. Finally, Schumacher (*58*) described the formation of ClO_3F in the thermal decomposition of Cl_2O_7 at 100° in the presence of fluorine. About 75% of the chlorine oxide is transformed into a mixture of ClO_3F and (less) ClO_2F. This is compatible with the thermal decomposition of Cl_2O_6 in presence of fluorine at 40°C, when Cl_2O_7 but no ClO_3F is formed. A temperature difference of about

60°C can cause very great changes in the separate rate constants and the mean life of excited molecules, so that the kinetics of the above reactions may be quite different.

The *structure* was determined from the infrared spectrum (*50, 118, 121*). The molecule possesses C_{3v} symmetry; the four peripheral atoms are bound to the central chlorine atom. It was concluded that the Cl-F and Cl-O distances in ClO_3F are smaller than in ClO_2 or ClO_2F, and that correspondingly the bond strength is greater. The same conclusion was reached from a study of the thermal decomposition, which is homogeneous and unimolecular (*71*).

The dipole moment is $0.023 \pm 0.003D$ and is thus smaller than that of any other polar substance (*131*). In addition, ClO_3F has the highest known resistance to electrical breakdown of any gas (about 40% higher than for SF_6). It is also not affected by high energy radiation and is thus suitable as an insulator in high voltage systems.

Most of the *physical properties* of ClO_3F are collected in Table V.

TABLE V

PHYSICAL PROPERTIES OF ClO_2F AND ClO_3F

	ClO_2F	ClO_3F
Melting point [°C]	−115 (*171*) (Crystallization point)	−146 (*50*) −147.75 (*100*)
Boiling point [°C]	−6 (*171*)	−46.7 (*50, 89*)
Vapor pressure	(see text) (*171*)	(see text) (*100*)
Trouton constant	23.2 (*171*)	
Heat of vaporization (kcal $mole^{-1}$)	6.2 (*171*)	4.61 (*23, 89*) 4.62 (*100*)
Heat of formation (kcal)		-5.12 ± 0.68 (*137*)
Spectra		Infrared (*50, 118, 121*) Raman (*148*) Microwave (*119*)

Vapor pressures, densities and critical data have also been determined (*52, 89*).

$$\begin{aligned}
\log p_{\text{mm}} &= 18.90112 - 1443.467/T - 4.09566 \log T \\
D\ (\text{gm cm}^{-1}) &= 2.266 - 1.603 \times 10^{-3}T - 4.080 \times 10^{-6}T^2 \\
T_{\text{crit}} &= 368.33 \pm 0.1°\text{K} \\
p_{\text{crit}} &= 53.0 \text{ atm}
\end{aligned}$$

2. Reactions of ClO_3F

Perchloryl fluoride is an extraordinarily stable substance. Hydrolysis (*50, 124*), which yields fluoride and perchlorate, can be effected only by concentrated caustic soda in a sealed tube at 200–300°C; only slight reaction occurs with water under the same conditions. In a strongly acid medium ClO_3F is able to oxidize iodide (*50, 52*):

$$ClO_3F + 8I^- + 6H^+ \rightarrow Cl^- + F^- + 4I_2 + 3H_2O.$$

The oxidizing action is also apparent in reactions with hydrogen-containing compounds. Thus the combustion of H_2, CH_4, NH_3, or H_2S is supported by ClO_3F (*120*) and its use in flame photometry has been suggested (*156*).

Reaction with metallic sodium or potassium commences at 300°C, but then proceeds vigorously (*50*). With ammonia ClO_3F interacts in the gaseous or liquid phase and also in aqueous solution. The product is the ammonium salt of the amide of perchloric acid (*50, 124*):

$$ClO_3F + 3NH_3 \rightarrow NH_4F + ClO_3NH_2{\cdot}NH_3\ (= ClO_3{\cdot}NH{\cdot}NH_4).$$

This may be isolated as the potassium salts $ClO_3{\cdot}NHK$ and ClO_3NK_2 or as the barium or silver salt. Both the silver salt ClO_3NHAg and the cesium salt are explosive (*50, 124*). Perchloryl fluoride and sodium amide do not react (*124*).

Whereas ClO_2F readily forms adducts or chloryl salts with various electrophilic fluorides, perchloryl fluoride is unable to do so. There is no evidence of compound formation with BF_3 (at −120°C), with AsF_5 (at −78°C) or with PF_5 (at −78° and +25°C). Conductivity measurements on mixtures of BF_3 or PF_5 with ClO_3F also show no measurable change of conductivity compared with pure perchloryl fluoride (*105*). There is also no reaction between SO_3 and ClO_3F at −75°C (*105*). There is only a single instance of the formulation of a perchloryl salt. Sprysskow (*190*) interpreted a product of the composition $2SO_3{\cdot}HClO_4$ which was obtained by the action of SO_3 on $HClO_4$ in chloroform, as $(ClO_3)^+(HS_2O_7)^-$.

The low reactivity of ClO_3F stems from its structure and electronic configuration. Thus in the first place it is isosteric with the perchlorate anion; the octet of electrons is complete and the molecule is coordinatively saturated. Exchange of O for F in ClO_4^- leads to no essential change in the molecular structure and the high symmetry is retained. Thus the infrared spectrum shows only slight deviations of the O-Cl-F angle from the value for a regular tetrahedral molecule. In keeping with this, the dipole moment is very small and the associated lack of a basic center explains the insolubility in liquid hydrogen fluoride and the lack of reaction with Lewis acids such as PF_5, BF_3, and SO_3.

The analogy to the perchlorate ion is still clearer in reduction reactions. Just as the ClO_4^- ion is reduced only in strongly acid solution, since the symmetry and high stability is lost by the addition of a proton (i.e., by formation of $HClO_4$), so reduction of ClO_3F to chloride (e.g., by iodide) takes place only in strongly acid solution.

F. Dichlorine Heptoxide Cl_2O_7

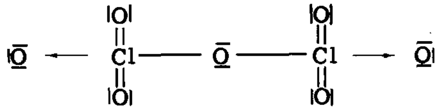
Dichlorine heptoxide is the anhydride of perchloric acid, and may be obtained in a pure state by dehydrating the concentrated acid with phosphorus pentoxide, followed by distillation between −38° and −34°C at 1 mm (*209*). Just as in the case of Cl_2O, the heptoxide appears to enter into an equilibrium with water. The equilibrium

$$2HClO_4 \rightleftharpoons Cl_2O_7 + H_2O \text{ (as } H_3OClO_4)$$

is indicated both by the fact that hydrated perchlorates of the transition metals result from interaction of anhydrous perchloric acid and transition metal chlorides (*81*) and also from studies of density for the system Cl_2O_7/H_2O (*149*).

Solid Cl_2O_7 is said to undergo a polymorphic transition at -100 ± 2°C (*209*). There is a simple eutectic with a melting point of −94°C in the system Cl_2O_7/CCl_4; the compounds are completely miscible above −23°C (*209*).

The structure of Cl_2O_7 has been discussed by Siebert (*188*). An approximate value of $N = 1.76$ for the outer ClO_3 groups (where N is bond order or multiplicity) has been obtained on the basis of calculation of the force constants from infrared spectral data. This value is probably somewhat too high as a result of uncertainty in the force constant calculation. It accords well with the assumption of a 5/3 bond order in the ClO_3 groups, so that the structure shown below is appropriate,



The bonds to the three outer oxygens are made equivalent by resonance, but the Cl-O-Cl group plays no part in this. Chlorine in dichlorine heptoxide thus has a dodecet of electrons. The central ∠Cl-O-Cl is 128° (*14*, *61*). A dipole moment of $0.72 \pm 0.02D$ has been found (*61*). The thermal decomposition of Cl_2O_7 in the gaseous state has been studied (*36*) at temperatures between 100° and 120°C at partial pressures of 1–80 mm with addition of Cl_2, O_2 and F_2 up to 400 mm in vessels of Pyrex and quartz.

III. Oxy-Compounds of Bromine

A. Dibromine Monoxide Br_2O

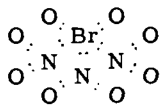
Dibromine monoxide was first isolated by Schwarz and Wiele (*182*, *183*) some time after it had been known in the form of its solution in carbon tetrachloride (*29*, *30*). Thermal decomposition of bromine dioxide in high vacuum yields, as Schwarz and Schmeisser also observed, (*184*), the components bromine and oxygen, a white oxide, and brown-black Br_2O, which may be obtained pure by subliming off bromine at −50°C. The white oxide is richer in oxygen than BrO_2 and Br_2O; it may be the white oxide BrO_3.

When slowly warmed at normal pressure dibromine monoxide melts at -17.5 ± 0.5°C with partial decomposition; it is completely stable at −40°C. Hydrolysis gives hypobromite, and Br_2O is thus the true anhydride of hypobromous acid (*30*). In carbon tetrachloride solution dibromine monoxide oxidises iodine to I_2O_5 (*183*).

B. Bromine Dioxide BrO_2

Bromine dioxide was first prepared by Schwarz and Schmeisser (*184*) in the glow discharge from a mixture of bromine and oxygen; BrO_2 separates in the discharge tube, which is cooled with liquid air. No ozone is formed if there is not too great an excess of oxygen. The solid yellow BrO_2 decomposes into its elements without melting when rapidly warmed to 0°C; when slowly warmed in vacuum, however, it gives dibromine monoxide among other products (see above, Section III,A). It is stable below −40°C, but decomposes when dissolved in carbon tetrachloride. The method of preparation in the discharge tube was improved later to give yields of 80% of BrO_2, based on the bromine used (*140*). The heat of formation of BrO_2 is -12.5 ± 0.7 kcal (*144*).

When nitrogen is added to the O_2-Br_2 mixture streaming through the discharge tube, the compound $BrO_2 \cdot 3NO_2$ separates in the discharge tube held at −186° (*145*). This is stable up to −50°C and may be sublimed in vacuum without decomposition. In its reaction with water and alkalis it behaves as a mixture of BrO_2 and NO_2. The compound $BrO_2 \cdot 3NO_2$ may also be obtained when excess of N_2O_4 is sublimed on to bromine dioxide held at −40°C and the temperature is then raised to −20°C. Excess of N_2O_4 may then be removed at −50°C (*145*). The structure shown below has been proposed*:



Schmeisser and Jörger (*165*) recently found that bromine dioxide could be prepared very conveniently by the low-temperature ozonization of bromine. Though reaction between bromine and ozone at room temperatures leads to higher oxides (see Section III,C) it is also possible to obtain BrO_2

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* Note added in proof: *Latest results show the structure of this compound to be* $BrNO_3 \cdot N_2O_5$ (M. Schmeisser and E. Schuster, unpublished).

under suitably controlled conditions. When an O_3-O_2 mixture, precooled to −78°C, is passed into a solution of bromine in a fluorochlorocarbon (e.g., $CFCl_3$, CF_2Cl_2) at −50°C, bromine is oxidized quantitatively to BrO_2, which may be obtained in a state of reasonable purity by distilling off the solvent

$$Br_2 + 4O_3 \rightarrow 2BrO_2 + 4O_2.$$

This method of low temperature ozonization may also be applied without difficulty to bromine compounds in which bromine is contained either in the cation or the anion. Thus bromine (I) nitrate at −78°C may be smoothly converted to bromyl nitrate (*159*):

$$BrNO_3 + 2O_3 \rightarrow BrO_2NO_3 + 2O_2$$

Bromine chloride at −60°C when treated with a stream of ozone gives bromine dioxide quantitatively (*90*).

$$2BrCl + 4O_3 \rightarrow 2BrO_2 + Cl_2 + 4O_2.$$

The possibility that the bromine chloride breaks down, and that the reaction is simply the ozonization of elementary bromine cannot, however, be excluded. Bromine dioxide mixed with iodine oxides also results if iodine bromide is used (*90*)

$$4IBr + 17O_3 \rightarrow 4BrO_2 + I_4O_9 + 17O_2.$$

A reaction of the same type occurs when ozone diluted with oxygen is passed into a solution of BrF_5 in liquid bromine at −5°C, when bromyl fluoride results (*166*).

$$BrF_5 + 2Br_2 + 10O_3 \rightarrow 5BrO_2F + 10O_2.$$

Bromine is initially oxidized to BrO_2 and this is then fluorinated by BrF_5 to BrO_2F (see below, Section III,D,*1*). Up to the present, apart from the reaction with N_2O_4, the only reaction of bromine dioxide which has been studied is its fluorination. This is discussed in the Section on BrO_2F.

C. HIGHER OXIDES

The action of ozone on bromine at room temperature leads to bromine oxides of various compositions. This thermal reaction was studied in detail as early as 1930 by Lewis, Schumacher and Feitnecht (*111–117*). The oxides formed had the composition $(Br_3O_8)_n$. Later Pflugmacher, using a greater ozone excess in the same reaction, obtained a compound $(BrO_3)_n$ (*146, 147*). This led Schumacher to reinvestigate the reaction (*6*). In a comprehensive investigation he examined the influence of the vessel material on the reaction and its products. Whereas the oxide obtained in quartz vessels had an oxygen-bromine ratio corresponding with the formula $(Br_3O_8)_n$, oxides with the formula $(Br_2O_6)_n$ were formed in Pyrex apparatus. It follows from these results that bromine oxides with a variable bromine:oxygen ratio result from the action of ozone on bromine at room temperature; the ratio of bromine to oxygen is greater than 1:2 and does not exceed 1:3. Which product is formed is determined by the material of the reaction vessel and possibly by the excess of ozone used.

The solid white oxides are stable at room temperature only in presence of ozone or atomic oxygen. The oxide Br_2O_5 dissolves in water to form bromic acid (*6*) and may therefore be the anhydride. Since, however, all these higher bromine oxides are polymeric it is not possible at present to decide to what extent they are mixtures or single compounds.

An oxide with the approximate composition BrO_3 was obtained by the interaction of Br_2 and O_2 in a glow discharge, using a fifty-fold excess of oxygen and a reaction temperature of $-10°$ to $+20°C$ (*146*). BrO_3 is also formed, at least superficially, when BrO_2 is treated with atomic oxygen (*146*); the oxide produced in addition to dibromine monoxide when BrO_2 decomposes may possibly also be BrO_3. The "BrO_3" stable below $-70°C$ dissolves in water to form a colorless solution:

$$2(BrO_3) + H_2O \rightarrow 2HBrO_3 + \tfrac{1}{2}O_2;$$

but there is no evidence for the formation of perbromic acid, $HBrO_4$.

D. Bromyl Fluoride BrO_2F (*141, 166, 167*)

1. *Formation and Preparation*

There had been several unsuccessful attempts to prepare oxyfluorides of bromine. Emeléus and Woolf (*47*), for example, on the basis of the analogy with the preparation of ClO_2F from potassium chlorate and bromine trifluoride, studied the action of BrF_3 on potassium bromate; only $KBrF_4$, bromine and oxygen were produced:

$$3KBrO_3 + 4BrF_3 \rightarrow 3KBrF_4 + 2Br_2 + \tfrac{9}{2}O_2.$$

When bromate is fluorinated with elementary fluorine at room temperature it is again found that only oxygen and bromine result, together with bromine trifluoride formed by reaction of the latter with fluorine (*122*).

Bromine dioxide is a suitable starting material for the preparation of BrO_2F: the reaction of fluorine with chlorine dioxide led to the first successful preparation of chloryl fluoride (*171*). Direct reaction with fluorine is not, however, practicable because reaction is exceedingly vigorous even at $-78°C$, possibly because of spontaneous decomposition of BrO_2. Explosions occurred on a number of occasions. Liquid chlorine or perfluoropentane, C_5F_{12}, proved to be a suitable diluent; BrO_2 is not soluble and must be suspended in the diluent, but it was found to be completely stable up to −40°C. When fluorine was passed slowly through a suspension of BrO_2 in C_5F_{12} at −50°C in a quartz flask, light yellow bromyl fluoride was formed.

$$BrO_2 + \tfrac{1}{2}F_2 \rightarrow BrO_2F.$$

It was only slightly soluble in perfluoropentane, and could be isolated by distilling off the diluent at −40°C in vacuum. It does not always deposit in a pure form.

In fluorinating BrO_2, fluorine may be replaced with advantage by bromine pentafluoride, the lower melting point of which (−61.4°C) gives better reaction conditions. At −55°C bromine dioxide reacts smoothly with liquid BrF_5 to form bromyl fluoride:

$$BrF_5 + 5BrO_2 \rightarrow 5BrO_2F + \tfrac{1}{2}Br_2.$$

After removal of bromine and unused BrF_5, the BrO_2F may be obtained pure by vacuum sublimation at −25°C.

Since the preparation of BrO_2F on a larger scale was only possible if bromine dioxide, which was available only in relatively small amounts, could be replaced by some other starting material, the fluorination of potassium bromate was reexamined (at the time the convenient method of oxidizing bromine with ozone in $CFCl_3$ was unknown). At −20° there was no reaction. Fluorsulfonic acid was also not suitable as potassium bromate dissolved in it only with complete decomposition, even at low temperatures.

As mentioned above, potassium bromate and bromine trifluoride at room temperature give only $KBrF_4$, bromine and oxygen; in bromine solution, on the other hand, reaction at the melting temperature of the BrF_3-Br_2 mixture proceeds primarily via bromyl fluoride:

$$3KBrO_3 + 5BrF_3 \rightarrow 3BrO_2F + \tfrac{3}{2}O_2 + 3KBrF_4 + Br_2.$$

A mixture of BrO_2F and BrF_3 was obtained from which it was difficult to obtain the former in a pure state by fractional distillation.

For preparative purposes, on the other hand, bromine pentafluoride may be used. At the melting point of BrF_5 (−61.4°C) the reaction

$$KBrO_3 + BrF_5 \rightarrow KBrF_4 + BrO_2F + \tfrac{1}{2}O_2$$

takes place with oxygen evolution and formation of bromyl fluoride. The conversion of $KBrO_3$ is 70%. Finally, this process led to the use of elementary bromine as the starting material. In passing a stream of ozone diluted with oxygen through a solution of bromine in BrF_5 at −5°C, BrO_2F is produced smoothly in the reaction

$$BrF_5 + 2Br_2 + 10O_3 \rightarrow 5BrO_2F + 10O_2.$$

This is a very convenient method for preparing BrO_2F. Bromyl fluoride is also formed together with ClO_2F in the reaction between BrF_5 and dichlorine hexoxide (*199*) and also in the analogous reaction of BrF_5 with dinitrogen pentoxide (*159*)

$$BrF_5 + 2Cl_2O_6 \rightarrow BrO_2F + 4ClO_2F + O_2$$

$$BrF_5 + 2N_2O_5 \rightarrow BrO_2F + 4NO_2F$$

2. Properties and Reactions of BrO_2F

The compound forms colorless crystals, which may be sublimed in vacuum at −25°C. Above its melting point (−9°C) it forms a colorless liquid which gradually becomes yellow at room temperature as the result of incipient decomposition. Vigorous decomposition occurs at +56°C, perhaps according to the equation

$$3BrO_2F \rightarrow BrF_3 + Br_2 + 3O_2$$

In the liquid state bromyl fluoride attacks glass fairly strongly and becomes reddish brown in color. It is decomposed explosively by water and reacts with organic substances with inflammation. In quartz ampoules BrO_2F may be kept indefinitely at temperatures below the melting point. Hydrolysis by excess of caustic soda solution at as low a temperature as possible is complete and leads to fluoride and bromate:

$$BrO_2F + 2OH^- \rightarrow BrO_3^- + F^- + H_2O.$$

There is a vigorous reaction with boron tribromide above −46°C, the melting point of the latter. However, only B_2O_3, BF_3, and Br_2 could be isolated from the products.

Besides BrO_2F the only bromyl compound known at present is bromyl nitrate, which is made from bromine(I) nitrate by ozonization at −78°C in $CFCl_3$ solution (see also Section III,B) (*159*). It is an orange colored powder which decomposes thermally according to the equation

$$BrO_2NO_3 \rightarrow \tfrac{1}{2}Br_2 + NO_2 + \tfrac{3}{2}O_2$$

and reacts at −78° with nitryl fluoride to form bromyl fluoride and dinitrogen pentoxide (*159*):

$$BrO_2NO_3 + NO_2F \rightarrow NO_2NO_3 + BrO_2F.$$

No fluorocomplexes could be obtained from BrO_2F and BF_3, AsF_5 or SbF_5.

IV. Oxy-Compounds of Iodine

It has so far been impossible to determine with certainty the number of oxides formed by iodine. Diiodine pentoxide, I_2O_5, is certainly well defined and behaves as the anhydride of iodic acid, but the other two oxides which have been isolated, I_2O_4 and I_4O_9, have not yet been unequivocally characterized, as least as far as their polymeric structures are concerned. Very recently intensive investigations have been commenced to determine their structures by means of spectroscopic studies. Salts of positive univalent iodine, such as I_2SO_4, may be regarded as derived formally from I_2O, though there is no indication of the existence of such an oxide. The iodine(I) salts will not be dealt with here.

A. DERIVATIVES OF DIIODINE TRIOXIDE I_2O_3

Diiodine trioxide has not yet been isolated in the free state, but it is said to occur as an intermediate in the thermal decomposition of I_2O_5 to iodine and oxygen. When I_2O_5 is heated with fuming sulfuric acid cationic tervalent iodine is stabilized as a salt which is stable at 220°C and one mole of oxygen is liberated (*132, 133*). One may assume an equilibrium of the type

$$2I_2 + 3I_2O_5 \rightleftharpoons 5I_2O_3$$

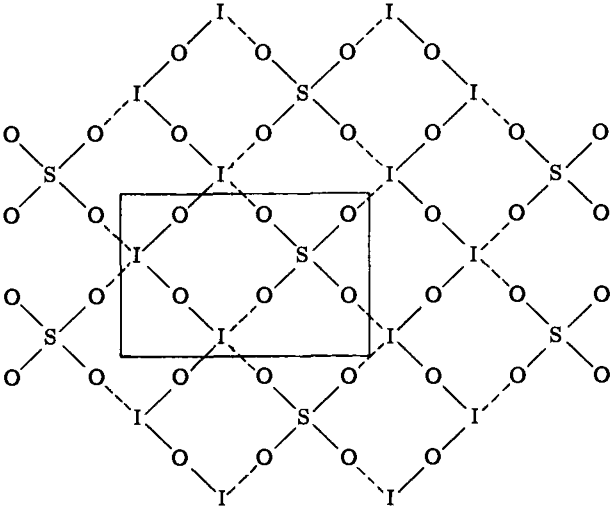
which is displaced to the right when an acid is added which is strong enough to form a salt with I_2O_3. In keeping with this iodosyl sulfate, $(IO)_2SO_4$, is obtained by simply shaking iodine with iodine pentoxide in concentrated sulfuric acid (*132, 133*). This yellow hygroscopic compound, which is also obtained by heating iodic acid with concentrated H_2SO_4, has been characterized by some other workers as a mono-hydrate (*12*) or a hemi-hydrate (*34, 55*). Hydrolysis occurs in water according to the equation (*92*)

$$5(IO)_2SO_4 + 8H_2O \rightarrow 2I_2 + 6HIO_3 + 5H_2SO_4.$$

A reaction occurs in essentially the same way when SO_3 reacts with a mixture of iodine and iodine pentoxide. A polysulfate $I_2O_3{\cdot}3SO_3$ results which, by analogy with the monosulfate, may be considered as diiodosyl trisulfate $(IO)_2S_3O_{10}$ (*110*). Direct reaction of SO_3 with I_2O_5 gives $I_2O_5{\cdot}2SO_3$ besides $I_2O_3{\cdot}3SO_3$.

A yellow crystalline compound which is also formed in the reaction of concentrated sulfuric acid with HIO_3 has been formulated as iodine(III) sulfate, $I_2(SO_4)_3$ (*93*). It is possible, however, to formulate this compound as an iodosyl trisulfate, a view which is supported by a method given in the literature (*56, 133*) for the preparation of the compound by reacting diiodosyl monosulfate with SO_3. Iodosyl nitrate, $IONO_3$, prepared from concentrated or anhydrous nitric acid and iodine (*92, 94*), has not yet been unambiguously characterized. Iodosyl selenate $(IO)_2SeO_4$, which is prepared from iodine, iodine pentoxide, and selenic acid, is very similar in its properties to the analogous sulfate, with which it is isomorphous (*38*).

The structures of iodosyl compounds have been investigated recently by Dasent and Waddington (*38*) from a study of infrared and visible spectra of iodosyl sulfate, selenate, and I_2O_4 (see Section IV,B). It was found that all four S-O and Se-O bonds are equivalent and that the tetrahedral symmetry of the sulfate and selenate groups is practically unchanged. The low value of the I-O stretching frequency, on the other hand, suggests a single bond. It was concluded that the structure probably consists of polymeric I-O chains, interspersed with sulfate and selenate groups, as shown in the Fig. 1. It is not possible to say if the SO_4 or SeO_4 groups are ionically or covalently bonded, though it is possible that the I---O-S bonds, shown in the figure by dotted lines, are bridging bonds. This interpretation accords with the fact that both iodosyl sulfate (*192*) and iodosyl selenate (*38*) are diamagnetic, though one would expect that the IO^+ cation, which is isoelectronic with the oxygen molecule, would be paramagnetic in the ground state (*192*). A polymeric structure is also in keeping with the insolubility of iodosyl compounds.



B. Diiodine Tetroxide I_2O_4

Diiodine tetroxide is prepared by the action of concentrated sulfuric acid on HIO_3 or a solid iodate (*12*, *136*) and is a yellow crystalline powder which is not hygroscopic. Thermal decomposition of I_2O_4 occurs rapidly at 135°C (*12*) according to the equation

$$5I_2O_4 \rightarrow 4I_2O_5 + I_2.$$

While I_2O_4 forms iodic acid and iodine when heated with water, the following reactions take place in alkaline or acid solution:

$$3I_2O_4 + 6OH^- \rightarrow 5IO_3^- + I^- + 3H_2O \text{ (}\mathit{136}\text{)}$$
$$I_2O_4 + 8H^+ + 8Cl^- \rightarrow 2ICl + 4H_2O + 3Cl_2.$$

Magnetic measurements (*202*) show I_2O_4 to be diamagnetic, but this indicates only that it is a polymer $(IO_2)_n$, where n must be an even number. The infrared investigations of Dasent and Waddington (*38*) have again given the first insight into the structure of this oxide, and shown it to be similar to that of iodosyl sulfate and selenate. The spectrum can be interpreted without difficulty on the assumption of a network of IO_3 groups and polymeric I-O chains, the two being linked by bonds with some degree of covalent character. On this basis I_2O_4 may be considered as iodosyl iodate, though it must be noted that no discrete IO^+ cations are present and that bonding to iodate occurs which has considerable covalent character.

Chemical evidence for the formulation of I_2O_4 as iodosyl iodate is provided by the hydrolysis of iodosyl sulfate. With excess of water, iodine, and iodic acid are formed (see Section IV,A), but, in moist air, I_2O_4 is formed in larger amounts. This can be interpreted in terms of a reaction between iodic acid formed in the hydrolysis with unchanged iodosyl sulfate, leading to I_2O_4 (*38*, *92*).

$$(IO)_2SO_4 + 2HIO_3 \rightarrow 2IOIO_3 + H_2SO_4.$$

A compound $I_2O_4{\cdot}3SO_3$ described by Muir more than 50 years ago (*136*) has been confirmed by Lehmann (*110*). This compound, obtained by the action of sulfur trioxide at 100°C according to the equation

$$I_2O_4 + 3SO_3 \rightarrow I_2O_4{\cdot}3SO_3,$$

may be regarded as iodosyl iodyl trisulfate, $(IO)(IO_2)(S_3O_{10})$. The same compound is formed by the action of ozone on iodine monochloride in a solution of SO_3 in HSO_3F (*199*). Diiodine tetroxide reacts with iodine pentafluoride to give iodoxy trifluoride (*8*) (see Section IV,D).

C. TETRAIODINE ENNEAOXIDE I_4O_9

The compound I_4O_9 may be made in two different ways. The first, the heating of concentrated phosphoric acid with HIO_3, is very similar to the preparation of I_2O_4 from iodic acid and concentrated sulfuric acid (*56*, *93*). The second method is by the reaction of ozone with iodine or compounds of univalent positive iodine. An oxygen-ozone mixture is either passed over heated iodine (*12*, *57*, *95*) or into a solution of iodine in chloroform or carbon tetrachloride at room temperature (*57*, *95*, *199*).

Ozone will oxidize iodine to I_4O_9 even at −78°C; thus, when a solution of iodine in $CFCl_3$ is dropped into a solution of ozone in the same solvent at −78°C and a pre-cooled O_2-O_3 stream is then passed, I_4O_9 is produced rapidly and quantitatively (*90*). The reaction of IBr with ozone to form I_4O_9 and BrO_2 is described under bromine dioxide.

Iodine monochloride also reacts with ozone at −78°C, though, in contrast to IBr, the molecule is not cleaved and a compound $I_2O_3Cl_2$ is formed (*90*).

$$2ICl + 3O_3 \rightarrow I_2O_3Cl_2 + 3O_2.$$

This may be a periodyl compound. Self-dissociation of iodine monochloride, according to the scheme $2ICl \rightleftharpoons I^+ + ICl_2^-$ postulated by Gutmann (*79*) in which chloride ion transfer occurs, is also probable in fluorochlorohydrocarbons. Attack of the iodide cation would then lead to a salt-like compound $[IO_3]^+[ICl_2]^-$, though this formula has not been verified by structural studies. The compound forms an adduct $I_2O_3Cl_2 \cdot 2C_5H_5N$ (m.p. 85°C) with pyridine and reacts with chlorine nitrate at −78°C according to the equation

$$I_2O_3Cl_2 + 2ClNO_3 \rightarrow I_2O_3(NO_3)_2 \text{ (or } [IO_3][I(NO_3)_2]) + 2Cl_2.$$

The oxychloride $I_2O_3Cl_2$ decomposes above −30°C to I_4O_9 and ICl_3 (*90*).

$$3I_2O_3Cl_2 \rightarrow I_4O_9 + 2ICl_3.$$

In keeping with this, ICl at 0°C may be ozonized directly to I_4O_9 (*199*); when ICl_3 is ozonized at 50–60°C, I_2O_5 is produced in addition to I_4O_9 (*199*). The yellow I_4O_9 is hygroscopic and decomposes at 75° (*12*):

$$4I_4O_9 \rightarrow 6I_2O_5 + 2I_2 + 3O_2.$$

It is commonly regarded as iodine(III) iodate, a formulation which is in keeping with the course of its hydrolysis:

$$\begin{array}{r}
5I(IO_3)_3 + 15H_2O \rightarrow 5I(OH)_3 + 15HIO_3 \\
5I(OH)_3 \rightarrow 3HIO_3 + I_2 + 6H_2O \\
\hline
5I(IO_3)_3 + 9H_2O \rightarrow 18HIO_3 + I_2
\end{array}$$

The reaction with anhydrous hydrogen fluoride is completely analogous:

$$I(IO_3)_3 + 3HF \rightarrow [IF_3] + 3HIO_3;$$

75% of the iodine appears as iodic acid (*199*). It is very probable that the reaction with hydrogen chloride follows the same scheme. Iodine trichloride results at −78°C, as would be expected from the equation

$$I(IO_3)_3 + 3HCl \rightarrow ICl_3 + 3HIO_3.$$

The quantity of ICl_3 is actually much larger than that corresponding with the equation since subsequent reaction of the iodic acid with HCl also gives iodine chlorides (*199*). These few reactions all indicate that I_4O_9 should be considered as $I(IO_3)_3$, but this formulation must be regarded as hypothetical as long as the structure has not been investigated.

D. DIIODINE PENTOXIDE I_2O_5

As the anhydride of iodic acid, I_2O_5 may be obtained from it by dehydration at 240–250°C.

$$2HIO_3 \rightarrow I_2O_5 + H_2O.$$

Another method of making the pentoxide is the ozonization of ICl_3 at 50–60°. As mentioned in the previous section much I_4O_9 is also produced (*199*). The oxide is also formed when iodine is passed through a glow discharge with oxygen and nitrogen (air) (*145*).

I_2O_5 is a white crystalline compound which decomposes at 300°C to iodine and oxygen. Structural information is given by the infrared spectrum, which shows $O_2I—O—IO_2$ units with an O atom bridging two IO_2 groups (*44*).

Diiodine pentoxide has oxidizing properties; NO is oxidized to N_2O_4 (and some N_2O_5) (*189*); C_2H_4 and H_2S are also oxidized (*173*). Sulfur trioxide forms an adduct at 100° (*110, 136, 196*):

$$I_2O_5 + 2SO_3 \rightarrow I_2O_5{\cdot}2SO_3\ [= (IO_2)_2(S_2O_7)].$$

This cannot be sublimed and decomposes at 130°C with loss of SO_3. Reaction with hydrogen chloride at its boiling point gives ICl_3 (*199*). I_2O_5 dissolves in liquid hydrogen fluoride; the reactions which occur are discussed under iodyl fluoride (see Section IV,E,*1*).

Fluorination of I_2O_5 leads as a rule to IF_5 and the action of elementary fluorine was investigated by Ruff (*154*):

$$I_2O_5 + 5F_2 \rightarrow 2IF_5 + \tfrac{5}{2}O_2$$

Other fluorinating agents which have been used are BrF_3 (*47, 139*), ClF_3 (*47*), SF_4 (*135*) and ClO_2F (*199*):

$$6I_2O_5 + 20BrF_3 \xrightarrow{\qquad} 12IF_5 + 10Br_2 + 15O_2$$

$$6I_2O_5 + 20ClF_3 \xrightarrow{\qquad} 12IF_5 + 10Cl_2 + 15O_2$$

$$I_2O_5 + 5SF_4 \xrightarrow{120^\circ} 2IF_5 + 5SOF_2$$

$$I_2O_5 + 10ClO_2F \xrightarrow{-50^\circ \text{ to } -20^\circ} 2IF_5 + 6ClO_2 + Cl_2O_6 + Cl_2O_7.$$

Iodine pentafluoride also reacts with I_2O_5. After the oxide has been dissolved in boiling IF_5, iodine oxytrifluoride separates as white needles on cooling to room temperature (*8*).

$$I_2O_5 + 3IF_5 \rightarrow 5IOF_3.$$

Contrary to the results of earlier workers (*155*), the reaction is not reversible. On warming to 110°C, IOF_3 undergoes a reversible change into IF_5 and iodyl fluoride

$$2IOF_3 \rightleftharpoons IF_5 + IO_2F$$

and the latter redissolves on boiling with IF_5 to form IOF_3 (*8*).

E. Iodyl Fluoride IO_2F (*105, 168*)

1. Preparation of IO_2F

Iodyl fluoride was first obtained by Aynsley, Nichols and Robinson by heating iodine oxytrifluoride, as described above (*8–10*). A convenient synthesis is the action of fluorine on a solution of iodic acid or iodine pentoxide in liquid hydrogen fluoride. The mechanism is discussed below.

Considerable evolution of heat occurs when HIO_3 or I_2O_5 is dissolved in hydrogen fluoride. If the pentoxide is considered as iodyl iodate, $IO_2^+IO_3^-$, then the large heat of solution may be considered as the sum of the heat of solution of iodic acid and the heat of the solvolysis reactions

$$IO_2IO_3 + HF \longrightarrow IO_2F + HIO_3$$

and

$$IO_2F \xrightarrow{HF} IO_2^+ + F^-.$$

This parallels the hydrolysis

$$IO_2IO_3 + H_2O \rightarrow IO_2OH + HIO_3\ (= 2HIO_3).$$

It has been possible to verify experimentally the formation of an equimolar mixture of IO_2F and HIO_3 on decomposing I_2O_5 with hydrogen fluoride.

Exploratory conductivity measurements have been made with solutions of iodic acid in hydrogen fluoride at different concentrations. Addition of HIO_3 to hydrogen fluoride causes a sudden increase in the electrical conductivity, indicating electrolytic dissociation of the iodic acid. This observation is in keeping with work of K. and H. Fredenhagen (*62–68*) on the liquid hydrogen fluoride solvent system. These authors also carried out conductivity measurements on solutions of inorganic and organic compounds and showed that practically all inorganic acids with the exception of complex fluoro acids function as bases in this solvent.

In an earlier section it was shown that perchloric acid, the strongest acid in water, is only an ampholyte in hydrogen fluoride, and has appreciable basic character. Iodic acid is likewise an acid of medium strength in water but functions as a base in hydrogen fluoride:

$$HIO_3 + HF \overset{HF}{\rightleftharpoons} (H_2IO_3)^+ + F^-.$$

Abstraction of water can also occur:

$$(H_2IO_3)^+ \overset{HF}{\rightleftharpoons} IO_2^+ + H_2O.$$

The fact that B_2O_3 is formed on passing boron trifluoride into a solution of HIO_3 in hydrogen fluoride indicates the correctness of the above scheme. At last IO_2^+ and F^- can react:

$$IO_2^+ + F^- \rightleftharpoons IO_2F.$$

Fluorine may be successfully used to remove water in preparative reactions in hydrogen fluoride

$$F_2 + H_2O \rightarrow 2HF + \tfrac{1}{2}O_2.$$

Thus after passing fluorine for several hours through a solution of HIO_3 or I_2O_5 in hydrogen fluoride and distilling off the solvent, iodyl fluoride is obtained in a very pure form after drying in vacuum at 50°C. The over-all reaction may be represented by the following equation:

$$I_2O_5 + F_2 \xrightarrow{HF} 2IO_2F + \tfrac{1}{2}O_2.$$

The colorless crystalline iodyl fluoride is completely stable at room temperature and is not particularly hygroscopic, though in moist air it evolves HF slowly. The decomposition temperature is not sharp; glass is attached at 210–230°C, iodine being set free.

2. Reactions of IO_2F; Iodyl Salts

Hydrolysis occurs, as would be expected, according to the equation (*8*)

$$IO_2F + 2OH^- \rightarrow IO_3^- + F^- + H_2O.$$

Ammonia, on the other hand, forms, in absence of light, a yellow-white compound of the composition $IO_2F\cdot 3NH_3$; on exposure to light a brownish-black inhomogeneous powder results, in which the ammonia and fluorine contents are lower.

Iodyl fluoride dissolves as a "base" in hydrogen fluoride and iodyl salts may be prepared by neutralization with compounds which function as acids in this system. With fluoroboric acid, obtained by passing BF_3 into the solution, a white crystalline $IO_2(BF_4)$ may be isolated. It is very readily soluble in hydrogen fluoride and decomposes again at 45°C into BF_3 and IO_2F. The behavior of AsF_5 or $HAsF_6$ is completely analogous: $IO_2(AsF_6)$ is obtained as a white crystalline powder when the hydrogen fluoride is distilled off. It is not possible to get $IO_2(AsF_4)$ with AsF_3 as reduction to iodine takes place. This redox reaction occurs very slowly, however, and the arsenic can be oxidized by passing in fluorine so that $IO_2(AsF_6)$ is again obtained. From these clear-cut reactions it is clear that we are dealing with true iodyl compounds and Aynsley's assumption (*11*) that the arsenic compound is $(AsF_4)^+(IO_2F_2)^-$ becomes less probable. If BF_3, $SiCl_4$, AsF_5, or SO_3 are passed directly over solid IO_2F no reaction results (*11*). A compound $IO_2F \cdot 0.8SbF_5$ was also obtained by Aynsley (*11*).

Iodyl fluoride functions in the hydrogen fluoride solvent system only as a weak base and no reaction could be detected with perchloric acid, which functions as an ampholyte. When IO_2F is heated under reflux with excess of sulfur trioxide the reaction is exactly like that of chloryl fluoride.

$$IO_2F + SO_3 \rightarrow IO_2SO_3F.$$

Iodyl fluoride reacts with N_2O_5 or anhydrous nitric acid to form I_2O_5, and behaves similarly with dichlorine hexoxide, though chloryl fluoride is also formed (*199*).

$$2IO_2F + 2Cl_2O_6 \rightarrow 2ClO_2F + I_2O_5 + 2ClO_2 + \tfrac{3}{2}O_2.$$

Strong fluorinating agents convert iodyl fluoride into iodine pentafluoride (*11*).

$$3IO_2F + 4BrF_3 \rightarrow 3IF_5 + 2Br_2 + 3O_2$$

$$IO_2F + 2SeF_4 \rightarrow IF_5 + 2SeOF_2$$

With 100% hydrogen peroxide reduction to elementary iodine occurs. Iodyl sulfates are considered under iodine oxides.

Conversely, IO_2F is also able to take up a fluoride ion. As early as 1899 Weinland, Lauenstein, and Köppen (*197*, *198*) obtained compounds of the type MIO_2F_2 (M = Na, K, Rb, Cs, NH_4) by evaporating solutions of the alkali iodate in 40% hydrofluoric acid. Investigation of the structure of the potassium salt KIO_2F_2 showed the presence of $IO_2F_2^-$ groups (*83*). Further reactions in which IO_2F reacts by taking up fluoride ions are not yet known.

F. PERIODYL FLUORIDE IO_3F (*105*, *168*)

1. *Preparation of* IO_3F

The analogous method to that used in preparing iodyl fluoride may be used to make this compound, *meta*- or *ortho*-periodic acid being decomposed by fluorine in anhydrous hydrogen fluoride:

$$HIO_4 + F_2 \xrightarrow{HF} IO_3F + HF + \tfrac{1}{2}O_2.$$

The mechanism discussed for the formation of IO_2F may be applied directly to this reaction, which can then be formulated as follows:

$$HIO_4 + HF \overset{HF}{\rightleftharpoons} (H_2IO_4)^+ + F^-$$

$$(H_2IO_4)^+ \overset{HF}{\rightleftharpoons} IO_3^+ + H_2O$$

$$IO_3^+ + F^- \rightleftharpoons IO_3F.$$

The water produced in the equilibrium reaction is taken up by fluorine. The preparation, like that of IO_2F is carried out in platinum apparatus. Since periodic acid is catalytically broken down to iodic acid and oxygen, the periodyl fluoride isolated is contaminated with IO_2F.

Periodyl fluoride is a white crystalline compound which is more stable to hydrolysis than IO_2F. It may be stored in glass vessels without decomposition. It decomposes at about 100°C to IO_2F and oxygen. Periodyl fluoride is soluble in hydrogen fluoride and in anhydrous hydrogen cyanide without decomposition.

2. Reactions of IO_3F

Periodyl fluoride dissolves slowly in caustic soda solution to form sodium periodate and sodium fluoride.

$$IO_3F + 2OH^- \rightarrow IO_4^- + F^- + H_2O.$$

Ammonia gives periodyl amide, which may be isolated as an ammoniate

$$IO_3F + 3NH_3 \rightarrow IO_3NH_2{\cdot}NH_3 + NH_4F$$

The amide shows remarkable thermal stability; it starts to turn brown at 185°C and decomposes spontaneously at 210°C. It decomposes in water to periodate and ammonia. This parallels the reaction of ammonia with ClO_3F (*50*), though in that case the ammonium salt $ClO_3NH{\cdot}NH_4$ is formed because of the acid character of the amide of perchloric acid. This salt is stable in aqueous solution.

The tendency to form complexes containing the periodyl cation, IO_3^+, is appreciably less than that for IO_2F, just as it is for ClO_3F compared with ClO_2F. Nevertheless, neutralization reactions may be carried out in hydrogen fluoride with IO_3F acting as a base. Thus, with HBF_4, $IO_3(BF_4)$ may be obtained as a colorless crystalline powder; in moist air it deliquesces to a brown mass. Reaction with $HAsF_6$ leads to a solvated product of composition $IO_3(AsF_6){\cdot}10HAsF_6$. Thermal degradation leads first of all to a product with $4HAsF_6$, but above 90°C decomposition occurs with loss of oxygen. Reaction with SO_3 at -10°C in $CFCl_3$ gives iodyl fluorosulfanate, with evolution of oxygen:

$$IO_3F + SO_3 \rightarrow IO_2SO_3F + \tfrac{1}{2}O_2.$$

Both AsF_3 and 100% H_2O_2 reduce IO_3F to elementary iodine.

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