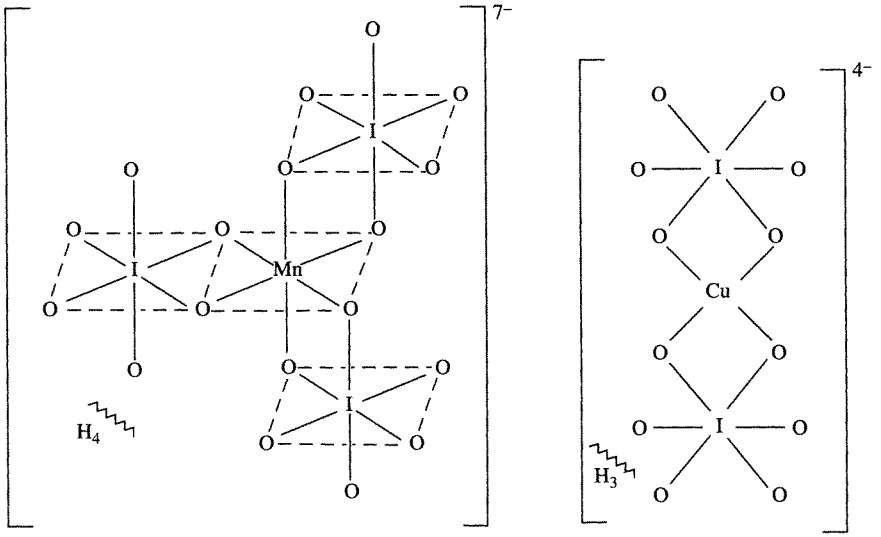


(a) $[H_4Mn(IO_6)_3]^{7-}$ (b) $[H_3Cu(IO_6)_2]^{4-}$

Figure 17.25 Structure of anions in $Na_7[H_4Mn(IO_6)_3].17H_2O$ and $Na_3K[H_3Cu(IO_6)_2].14H_2O$.

formation of the cyclic intermediate. Such reactions have been widely used in carbohydrate and nucleic acid chemistry.

Periodates form numerous complexes with transition metals in which the octahedral IO_6^{5-} unit acts as a bidentate chelate. Examples are:

$[Mn^{IV}(IO_6)]^-$, $[Ni^{IV}(IO_6)]^-$, $[Fe^{III}(IO_6)]^{2-}$, $[Co^{III}(IO_6)]^{2-}$
$[M^{IV}(IO_6)_2]^{6-}$ (M^{IV} = Pd, Pd, Ce);
$[M^{III}(IO_6)_2]^{7-}$ (M^{III} = Fe, Co, Cu, Ag, Au)
$[Mn^{IV}(IO_6)_3]^{11-}$; $[Fe^{III}_4(IO_6)_3]^{3-}$, $[Co^{III}_4(IO_6)_3]^{3-}$

The stabilization of Ni^{IV}, Cu^{III} and Ag^{III} is notable and many of the complexes have very high formation constants, e.g. $[Cu(IO_6)_2]^{7-} \sim 10^{10}$, $[Co(IO_6)_2]^{7-} \sim 10^{18}$. The high formal charge on the anion is frequently reduced by protonation of the $\{I(\mu\text{-}O)_2O_4\}$ moiety, as in orthoperiodic acid itself. For example $H_{11}[Mn(IO_6)_3]$ is a heptabasic acid with pK_1 and $pK_2 < 0$, pK_3 2.75, pK_4 4.35, pK_5 5.45, pK_6 9.55, and pK_7 10.45. The crystal structure of $Na_7[H_4Mn(IO_6)_3].17H_2O$ features a 6-coordinate paramagnetic Mn^{IV} anion (Fig. 17.25a) whereas the diamagnetic compound $Na_3K[H_3Cu(IO_6)_2]$-$14H_2O$ has square-planar Cu^{III} (Fig. 17.25b).

17.2.9 Halogen oxide fluorides and related compounds[146]

This section considers compounds in which X (Cl, Br or I) is bonded to both O and F, i.e. F_nXO_m. Oxofluorides –OF and peroxofluorides –OOF have already been discussed (p. 638) and halogen derivatives of oxoacids, containing –OX bonds are treated in the following section (p. 883).

Chlorine oxide fluorides[147]

Of the 6 possible oxide fluorides of Cl, 5 have been characterized: they range in stability from the thermally unstable $FCl^{III}O$ to the chemically rather inert perchloryl fluoride $FCl^{VII}O_3$. The others are $FCl^{V}O_2$, $F_3Cl^{V}O$ and $F_3Cl^{VII}O_2$.

[146] Ref. 23, pp. 1386–96, The oxyfluorides of the halogens.
[147] K. O. CHRISTE and C. J. SCHACK, *Adv. Inorg. Chem. Radiochem.* **18**, 319–98 (1976).

The remaining compound $F_5Cl^{VII}O$ has been claimed but the report could not be confirmed. Fewer bromine oxide fluorides are known, only $FBrO_2$, F_3BrO and possibly $FBrO_3$ being characterized. The compounds of iodine include the I^V derivatives FIO_2 and F_3IO and the I^{VII} derivatives FIO_3, F_3IO_2 and F_5IO. All the halogen oxide fluorides resemble the halogen fluorides (p. 824), to which they are closely related both structurally and chemically. Thus they tend to be very reactive oxidizing and fluorinating agents and several can act as Lewis acids or bases (or both) by gain or loss of fluoride ions, respectively.

The structures of the chlorine oxide fluorides are summarized in Fig. 17.26, together with those of related cationic and anionic species formed from the neutral molecules by gain or loss or F^-. The first conclusive evidence for free FClO in the gas phase came in 1972 during a study of the hydrolysis of ClF_3 with substoichiometric amounts of H_2O in a flow reactor:

$$ClF_3 + H_2O \longrightarrow FClO + 2HF$$

The compound is thermally unstable, and decomposes with a half-life of about 25 s at room temperature:

$$2FClO \xrightarrow{\text{rt}/t_{\frac{1}{2}}\ 25\text{ s}} FClO_2 + ClF$$

The compound can also be made by photolysis of a mixture of ClF and O_3 in Ar at 4–15 K; evidence for the expected nonlinear by structure comes from vibration spectroscopy (Fig. 17.26a).

F_3ClO was discovered in 1965 but not published until 1972 because of US security classification. It has low kinetic stability and is an extremely powerful fluorinating and oxidizing agent. It can be made in yields of up to 80% by fluorination of Cl_2O in the presence of metal fluorides, e.g. NaF:

$$Cl_2O + 2F_2 \xrightarrow[-78°]{\text{MF}} F_3ClO + ClF$$

However, the unpredictably explosive nature of Cl_2O in the liquid state renders this process somewhat hazardous and the best large-scale preparation is the low-temperature fluorination of $ClONO_2$ (p. 884):

$$ClONO_2 + 2F_2 \xrightarrow[(>80\%\text{ yield})]{-35°} F_3ClO + FNO_2$$

F_3ClO is a colourless gas or liquid: mp −43°, bp 28° d(l, 20°) 1.865 g cm^{-3}. The compound

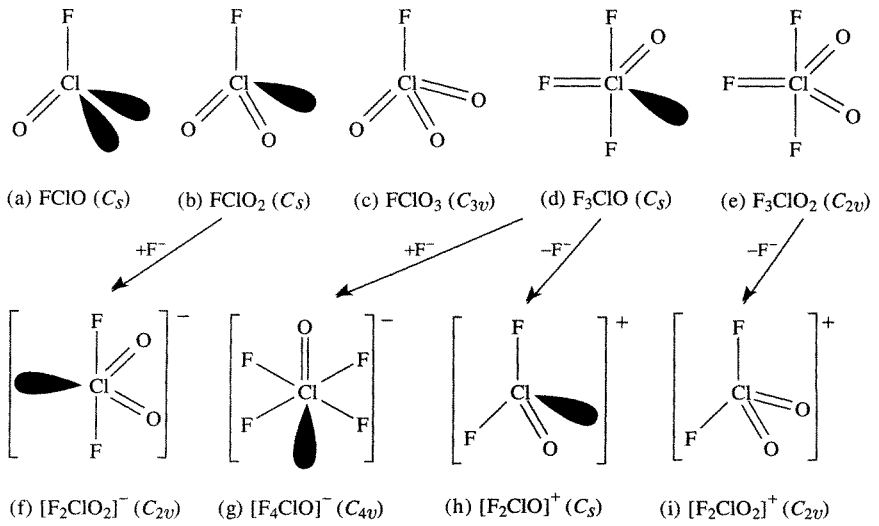


Figure 17.26 Structures of chlorine oxide fluorides and related cations and anions.

is stable at room temperature: $\Delta H_f^\circ(g) = -148\,kJ\,mol^{-1}$, $\Delta H_f^\circ(l) = -179\,kJ\,mol^{-1}$. Its C_s structure (Fig. 17.26d) has been established by gas electron diffraction which also led to the dimensions Cl=O 140.5 pm, Cl–F_{eq} 160.3 pm, Cl–F_{ax} 171.3 pm, and angle F_{ax}–Cl–F_{ax} 171°; other angles are F_{ax}–Cl–F_{eq} 88°, F_{ax}–Cl–O 95° and F_{eq}–Cl–O 109°.[148] F_3ClO can be handled in well-passivated metal, Teflon or Kel-F but reacts rapidly with glass or quartz. Its thermal stability is intermediate between those of ClF_3 and ClF_5 (p. 832) and it decomposes above 300°C according to

$$F_3ClO \longrightarrow ClF_3 + \tfrac{1}{2}O_2$$

F_3ClO tends to react slowly at room temperature but rapidly on heating or under ultraviolet irradiation. Typical of its fluorinating reactions are:

$$Cl_2 + F_3ClO \xrightarrow{200^\circ} 3ClF + \tfrac{1}{2}O_2$$

$$Cl_2O + F_3ClO \xrightarrow{rt} 2ClF + FClO_2$$

$$ClOSO_2F + F_3ClO \longrightarrow SO_2F_2 + FClO_2 + ClF$$

$$2ClOSO_2F + F_3ClO \longrightarrow S_2O_5F_2 + FClO_2 + 2ClF$$

Combined fluorinating and oxygenating capacity is exemplified by the following (some of the reactions being complicated by further reaction of the products with F_3ClO):

$$SF_4 + F_3ClO \xrightarrow{CsF/25^\circ} SF_6, FClO_2, SF_5Cl, SF_4O$$

$$MoF_5 + F_3ClO \longrightarrow MoF_6, MF_4O$$

$$2N_2F_4 + F_3ClO \xrightarrow{100^\circ} 3NF_3 + FNO + ClF$$

$$HNF_2 + F_3ClO \xrightarrow{\text{low temp}} NF_3O, NF_2Cl, N_2F_4, FClO_2, HF$$

$$F_2NC(O)F + F_3ClO \longrightarrow NF_3O, ClNF_2, N_2F_4$$

It reacts as a reducing agent towards the extremely strong oxidant PtF_6:

$$F_3ClO + PtF_6 \longrightarrow [F_2ClO]^+[PtF_6]^- + \tfrac{1}{2}F_2$$

Hydrolysis with small amounts of water yields HF but this can react further by fluoride ion abstraction:

$$F_3ClO + H_2O \longrightarrow FClO_2 + 2HF$$

$$F_3ClO + HF \longrightarrow [F_2ClO]^+[HF_2]^-$$

This last reaction is typical of many in which F_3ClO can act as a Lewis base by fluoride ion donation to acceptors such as MF_5 (M = P, As, Sb, Bi, V, Nb, Ta, Pt, U), MoF_4O, SiF_4, BF_3, etc. These products are all white, stable, crystalline solids (except the canary yellow PtF_6^-) and contain the $[F_2ClO]^+$ cation (see Fig. 17.26h) which is isostructural with the isoelectronic F_2SO. Chlorine trifluoride oxide can also act as a Lewis acid (fluoride ion acceptor) and is therefore to be considered as amphoteric (p. 225). For example KF, RbF and CsF yield $M^+[F_4ClO]^-$ as white solids whose stabilities increase with increasing size of M^+. Vibration spectroscopy establishes the C_{4v} structure of the anion (Fig. 17.29g).

The other Cl^V oxide fluoride $FClO_2$ (1942) can be made by the low-temperature fluorination of ClO_2 but is best prepared by the reaction:

$$6NaClO_3 + 4ClF_3 \xrightarrow[\text{(high yield)}]{\text{rt/1 day}} 6FClO_2 + 6NaF + 2Cl_2 + 3O_2$$

The C_s structure and dimensions (Fig. 17.26b) were established by microwave spectroscopy which also yielded a value for the molecular dipole moment μ 1.72 D. Other physical properties of this colourless gas are mp −115° (or −123°), bp ~ −6°, $\Delta H_f^\circ(g, 298\,K)$ $-34 \pm 10\,kJ\,mol^{-1}$ [or $-273\,kJ\,mol^{-1}$ when corrected for $\Delta H_f^\circ(HF, g)$!]. $FClO_2$ is thermally stable at room temperature in dry passivated metal containers and quartz. Thermal decomposition of the gas (first-order kinetics) only becomes measurable above 300° in quartz and above 200° in Monel metal:

$$FClO_2(g) \xrightarrow{300^\circ} ClF(g) + O_2(g)$$

It is far more chemically reactive than $FClO_3$ (p. 879) despite the lower oxidation state of Cl.

[148] H. OBERHAMMER and K. O. CHRISTIE, *Inorg. Chem.* **21**, 273–5 (1982).

Hydrolysis is slow at room temperature and the corresponding reaction with anhydrous HNO_3 results in dehydration to the parent N_2O_5:

$$2FClO_2 + H_2O \longrightarrow 2HF + 2ClO_2 + \tfrac{1}{2}O_2$$

$$2FClO_2 + 2HONO_2 \longrightarrow 2HF + 2ClO_2 + \tfrac{1}{2}O_2 + N_2O_5$$

Other reactions with protonic reagents are:

$$2OH^-(aq) + FClO_2 \longrightarrow ClO_3^- + F^- + H_2O$$

$$NH_3(l) + FClO_2 \xrightarrow[\text{ignites}]{-78^\circ} NH_4Cl, NH_4F$$

$$HCl(l) + FClO_2 \xrightarrow{-110^\circ} HF + ClO_2 + \tfrac{1}{2}Cl_2$$

$$HOSO_2F + FClO_2 \xrightarrow{-78^\circ} HF + ClO_2OSO_2F$$

$$HOClO_3(\text{anhydrous}) + FClO_2 \longrightarrow HF + ClO_2OClO_3$$

$$SO_3 + FClO_2 \xrightarrow{-10^\circ} ClO_2OSO_2F \text{ (insertion)}$$

$FClO_2$ explodes with the strong reducing agent SO_2 even at -40° and HBr likewise explodes at -110°.

Chlorine dioxide fluoride is a good fluorinating agent and a moderately strong oxidant: SF_4 is oxidized to SF_6, SF_4O and SF_2O_2 above 50°, whereas N_2F_4 yields NF_3, FNO_2 and FNO at 30°. UF_4 is oxidized to UF_5 at room temperature and to UF_6 at 100°. Chlorides (and some oxides) are fluorinated and the products can react further to form fluoro complexes. Thus, whereas $AlCl_3$ yields AlF_3, B_2O_3 affords $[ClO_2]^+BF_4^-$, and the Lewis acid chlorides $SbCl_5$, $SnCl_4$ and $TiCl_4$ yield $[ClO_2]^+[SbF_6]^-$, $[ClO_2]^+_2[SnF_6]^{2-}$ and $[ClO_2]^+_2[TiF_6]^{2-}$. Such complexes, and many others can, of course, be prepared directly from the corresponding fluorides either with or without concurrent oxidation, e.g.:

$$AsF_3 + 3FClO_2 \longrightarrow [ClO_2]^+[AsF_6]^- + 2ClO_2$$

$$SbF_5 + FClO_2 \longrightarrow [ClO_2]^+[SbF_6]^- \text{ (mp 220°)}$$

$$2SbF_5 + FClO_2 \longrightarrow [ClO_2]^+[Sb_2F_{11}]^-$$

An X-ray study on this last compound showed the chloryl cation to have the expected nonlinear structure, with angle OClO 122° and Cl–O 131 pm. $FClO_2$ can also act as a fluoride ion acceptor, though not so readily as F_3ClO above. For example CsF reacts at room temperature to give the white solid $Cs[F_2ClO_2]$; this is stable at room temperature but dissociates reversibly into its components above 100°. The C_{2v} structure of $[F_2ClO_2]^-$ (Fig. 17.26f) is deduced from its vibration spectrum.

The two remaining Cl^{VII} oxide fluorides are F_3ClO_2 and $FClO_3$. At one time F_3ClO_2 was thought to exist in isomeric forms but the so-called violet form, previously thought to be the peroxo compound F_2ClOOF has now been discounted.[147] The well-defined compound F_3ClO_2 was first made in 1972 as an extremely reactive colourless gas: mp -81.2°, bp -21.6°. It is a very strong oxidant and fluorinating agent and, because of its corrosive action, must be handled in Teflon or sapphire apparatus. It thus resembles the higher chlorine fluorides. The synthesis of F_3ClO_2 is complicated and depends on an ingenious sequence of fluorine-transfer reactions as outlined below:

$$2FClO_2 + 2PtF_6 \longrightarrow \underbrace{[F_2ClO_2]^+[PtF_6]^- + [ClO_2]^+[PtF_6]^-}_{2FNO_2} \longrightarrow F_3ClO_2 + FClO_2 + 2[NO_2]^+[PtF_6]^-$$

Fractional condensation at -112° removes most of the $FClO_2$, which is slightly less volatile than F_3ClO_2. The remaining $FClO_2$ is removed by complexing with BF_3 and then relying on the greater stability of the F_3ClO_2 complex:

$$\left.\begin{matrix} FClO_2 \\ \text{(mixture)} \\ F_3ClO_2 \end{matrix}\right\} + 2BF_3 \longrightarrow \begin{cases} [ClO_2]^+[BF_4]^- \text{ (dissoc press 1 atm at 44°C)} \\ [F_2ClO_2]^+[BF_4]^- \text{ stable at room temperature} \end{cases}$$

Pumping at 20° removes $[ClO_2]^+[BF_4]^-$ as its component gases, leaving $[F_2ClO_2]^+[BF_4]^-$ which, on treatment with FNO_2, releases the

desired product:

$$[F_2ClO_2]^+[BF_4]^- + FNO_2 \longrightarrow [NO_2]^+[BF_4]^- + F_3ClO_2$$

The whole sequence of reactions represents a *tour de force* in the elegant manipulation of extremely reactive compounds. F_3ClO_2 is a violent oxidizing reagent but forms stable adducts by fluoride ion transfer to Lewis acids such as BF_3, AsF_5 and PtF_6. The structures of F_3ClO_2 and $[F_2ClO_2]^+$ have C_{2v} symmetry as expected (Fig. 17.26e and i).

In dramatic contrast to F_3ClO_2, perchloryl fluoride ($FClO_3$) is notably inert, particularly at room temperature. This colourless tetrahedral molecular gas (Fig. 17.26c) was first synthesized in 1951 by fluorination of $KClO_3$ at $-40°$ and it can also be made (in 50% yield) by the action of F_2 on an aqueous solution of $NaClO_3$. Electrolysis of $NaClO_4$ in anhydrous HF has also been used but the most convenient route for industrial scale manufacture is the fluorination of a perchlorate with SbF_5, SbF_5/HF, $HOSO_2F$ or perhaps best of all $HOSO_2F/SbF_5$:

$$KClO_4 \xrightarrow[\text{rt (or above)}]{HOSO_2F/SbF_5} FClO_3 \quad (97\%\ \text{yield})$$

Because of its remarkably low reactivity at room temperature and its very high specific impulse, the gas has been much studied as a rocket propellent oxidizer (e.g. it compares favourably with N_2O_4 and with ClF_3 as an oxidizer for fuels such as N_2H_4, Me_2NNH_2 and LiH). $FClO_3$ has mp $-147.8°$, bp $-46.7°$, d(l, $-73°C$) 1.782 g cm^{-3}, viscosity $\eta(-73°)$ 0.55 centipoise. The extremely low dipole moment ($\mu = 0.023$ D) is particularly noteworthy. $FClO_3$ has high kinetic stability despite its modest thermodynamic instability: ΔH_f°(g, 298 K) -23.8 kJ mol^{-1}, ΔG_f°(g, 298 K) $+48.1$ kJ mol^{-1}. $FClO_3$ offers the highest known resistance to dielectric breakdown for any gas (30% greater than for SF_6, p. 687) and has been used as an insulator in high-voltage systems.

Perchloryl fluoride is thermally stable up to about 400°. Above 465° it undergoes decomposition with first-order kinetics and an activation energy of 244 kJ mol^{-1}. Hydrolysis is slow even at 250–300° and quantitative reaction is only achieved with concentrated aqueous hydroxide in a sealed tube under high pressure at 300°C:

$$FClO_3 + 2NaOH \longrightarrow NaClO_4 + NaF + H_2O$$

However, alcoholic KOH effects a similar quantitative reaction at 25°C. Reaction with liquid NH_3 is also smooth particularly in the presence of a strong nucleophile such as $NaNH_2$:

$$FClO_3 + 3NH_3 \longrightarrow [NH_4]^+[HNClO_3]^- + NH_4F$$

Metallic Na and K react only above 300°.

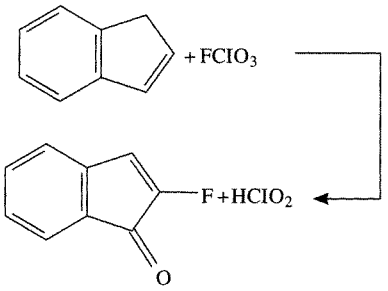
$FClO_3$ shows no tendency to form adducts with either Lewis acids or bases. This is in sharp contrast to most of the other oxide fluorides of chlorine discussed above and has been related to the preferred tetrahedral (C_{3v}) geometry as compared with the planar (D_{3h}) and trigonal bipyramidal (D_{3h}) geometries expected for $[ClO_3]^+$ and $[F_2ClO_3]^-$ respectively. Conversely the pseudo-trigonal bipyramidal C_s structure F_3ClO gains stability when converted to the pseudo-tetrahedral $[F_2ClO]^+$ or pseudo-octahedral $[F_4ClO]^-$ (see Fig. 17.26).

In reactions with organic compounds $FClO_3$ acts either as an oxidant or as a 1- or 2-centre electrophile which can therefore be used to introduce either F, a $-ClO_3$ group, or both F and O into the molecule. As $FClO_3$ is highly susceptible to nucleophilic attack at Cl it reacts readily with organic anions:

$$FClO_3 + Li^+Ph^- \longrightarrow PhClO_3 + LiF$$

$$FClO_3 + Li^+[C_4H_3S]^- \longrightarrow \text{(2-fluorothiophene)} + LiClO_3$$

Compounds having a cyclic double bond conjugated to an aromatic ring (e.g. indene) undergo oxofluorination, with $FClO_3$ acting as a 2-centre electrophile:



$FClO_3$ also acts as a mild fluorinating agent for compounds possessing a reactive methylene group, e.g.:

$$CH_2(CO_2R)_2 \xrightarrow{FClO_3} CF_2(CO_2R)_2$$

It is particularly useful for selective fluorination of steroids.

Bromine oxide fluorides[149]

These compounds are less numerous and rather less studied than their chlorine analogues; indeed, until fairly recently only $FBrO_2$ was well characterized. The known species are:

Oxidation state of Br	Cations	**Neutral species**	Anions
V	$[BrO_2]^+$	**$FBrO_2$** (1955)	$[F_2BrO_2]^-$
	$[F_2BrO]^+$	**F_3BrO** (1976)	$[F_4BrO]^-$
VII		**$FBrO_3$** (1969)	

Despite several attempts at synthesis, there is little or no evidence for the existence of FBrO, F_3BrO_2 or F_5BrO. The bromine oxide fluorides are somewhat less thermally stable than their chlorine analogues and somewhat more reactive chemically. The structures are as already described for the chlorine oxide fluorides (Fig. 17.26).

Bromyl fluoride, $FBrO_2$, is a colourless liquid, mp $-9°$, which attacks glass at room temperature and which undergoes rapid decomposition above 55°:

$$3FBrO_2 \xrightarrow{\Delta} BrF_3 + Br_2 + 3O_2$$

It is best prepared by fluorine transfer reactions such as

$$K[F_2BrO_2] + HF(l) \longrightarrow KHF_2 + FBrO_2$$

The $K[F_2BrO_2]$ can be prepared by fluorination of $KBrO_3$ with BrF_5 in the presence of a trace of HF:

$$KBrO_3 + BrF_5 \longrightarrow FBrO_2 + K[F_4BrO]$$

$$K[F_4BrO] + KBrO_3 \longrightarrow 2K[F_2BrO_2]$$

However, the most convenient method of preparation of $K[F_2BrO_2]$ is by reaction of $KBrO_3$ with $KBrF_6$ in MeCN:

$$KBrO_3 + KBrF_6 \xrightarrow{MeCN} K[F_2BrO_2]\downarrow + K[F_4BrO]\ (sol)$$

Bromyl fluoride is also produced by fluorine-oxygen exchange between BrF_5 and oxoiodine compounds (p. 881), e.g.:

$$FIO_2 + BrF_5 \longrightarrow FBrO_2 + IF_5$$

$$2F_3IO + BrF_5 \longrightarrow FBrO_2 + 2IF_5$$

$$2I_2O_5 + 5BrF_5 \longrightarrow 5FBrO_2 + 4IF_5$$

As with $FClO_2$ and FIO_2, hydrolysis regenerates the halate ion, the reaction with $FBrO_2$ being of explosive violence. Hydrolysis in basic solution at 0° can be represented as

$$FBrO_2 + 2OH^- \longrightarrow BrO_3^- + F^- + H_2O$$

Organic substances react vigorously, often enflaming. Co-condensation of $FBrO_2$ with the Lewis acid AsF_5 produced $[BrO_2]^+[AsF_6]^-$. Vibrational spectra establish the expected non-linear structure of the cation (3 bands active in both Raman and infrared). $FBrO_2$ can also react as a fluoride ion acceptor (from KF).

Bromine oxide trifluoride, F_3BrO, is made by reaction of $K[F_4BrO]$ with a weak Lewis acid:

$$K[F_4BrO] + [O_2]^+[AsF_6]^- \longrightarrow F_3BrO + KAsF_6 + O_2 + \tfrac{1}{2}F_2$$

$$K[F_4BrO] + HF(anhydr) \xrightarrow{-72°} F_3BrO + KHF_2$$

[149] R. J. GILLESPIE and P. H. SPEKKENS, *Israel J. Chem.* **17**, 11–19 (1978). R. BOUGON, T. B. HUY, P. CHARPIN, R. J. GILLESPIE and P. H. SPEKKENS, *J. Chem. Soc., Dalton Trans.*, 6–12 (1979).

The product is a white solid which melts to a clear liquid at about −5°; it is only marginally stable at room temperature and slowly decomposes with loss of oxygen:

$$F_3BrO \longrightarrow BrF_3 + \tfrac{1}{2}O_2$$

The molecular symmetry is C_s (like F_3ClO; Fig. 17.26d) and there is some evidence for weak intermolecular association via $F_{ax}–Br\cdots F_{ax}$ bonding. Fluoride ion transfer reactions have been established and yield compounds such as $[F_2BrO]^+[AsF_6]^-$, $[F_2BrO]^+[BF_4]^-$ and $K[F_4BrO]$, though this last compound is more conveniently made independently, e.g. by the reaction of $KBrO_3$ with $KBrF_6$ mentioned above, or by direct fluorination of $K[F_2BrO_2]$:

$$K[F_2BrO_2] + F_2 \longrightarrow K[F_4BrO] + \tfrac{1}{2}O_2$$

Perbromyl fluoride, $FBrO_3$, is made by fluorinating the corresponding perbromate ion with AsF_5, SbF_5, BrF_5 or $[BrF_6]^+[AsF_6]^-$ in HF solutions. The reactions are smooth and quantitative at room temperature:

$$KBrO_4 + 2AsF_5 + 3HF \longrightarrow FBrO_3 + [H_3O]^+[AsF_6]^- + KAsF_6$$

$$2KBrO_4 + BrF_5 + 2HF \longrightarrow 2FBrO_3 + FBrO_2 + 2KHF_2$$

$$KBrO_4 + [BrF_6]^+[AsF_6]^- \longrightarrow FBrO_3 + BrF_5 + \tfrac{1}{2}O_2 + KAsF_6$$

Perbromyl fluoride is a reactive gas which condenses to a colourless liquid (bp 2.4°) and then solidifies to a white solid (mp *ca.* −110°). It has the expected C_{3v} symmetry Fig. 17.27 and decomposes slowly at room temperature; it is more reactive than $FClO_3$ and, unlike that compound, it reacts rapidly with water, aqueous base and even glass:

$$FBrO_3 + H_2O \longrightarrow BrO_4^- + HF + H^+$$

$$FBrO_3 + 2OH^- \longrightarrow BrO_4^- + F^- + H_2O$$

Fluoride ion transfer reactions have not been established for $FBrO_3$ and may be unlikely, (see p. 879).

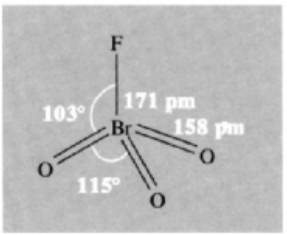


Figure 17.27 Structure of $FBrO_3$ as determined by gas-phase electron diffraction.

Iodine oxide fluorides

The compounds to be considered are the I^V derivatives FIO_2 and F_3IO and the I^{VII} derivatives FIO_3, F_3IO_2 and F_5IO. Note that, unlike Cl, no I^{III} compound FIO has been reported and that, conversely, F_5IO (but not F_5ClO) has been characterized.

FIO_2 has been prepared both by direct fluorination of I_2O_5 in anhydrous HF at room temperature and by thermal dismutation of F_3IO:

$$I_2O_5 + F_2 \xrightarrow{HF/20°} 2FIO_2 + \tfrac{1}{2}O_2$$

$$2F_3IO \xrightarrow{110°} FIO_2 + IF_5$$

Unlike gaseous molecular $FClO_2$, it is a colourless polymeric solid which decomposes without melting when heated above 200°. Like the other halyl fluorides it readily undergoes alkaline hydrolysis and also forms a complex with F^-:

$$FIO_2 + 2OH^- \longrightarrow IO_3^- + F^- + H_2O$$

$$FIO_2 + KF \xrightarrow{HF} K^+[F_2IO_2]^-$$

An X-ray study of this latter complex reveals a C_{2v} anion as in the chlorine analogue (Fig. 17.28a). This is closely related to the C_s structure of the neutral molecule F_3IO (Fig. 17.28b).

F_3IO is prepared as colourless crystals by dissolving I_2O_5 in boiling IF_5 and then cooling the mixture:

$$I_2O_5 + 3IF_5 \xrightarrow{105°} 5F_3IO$$

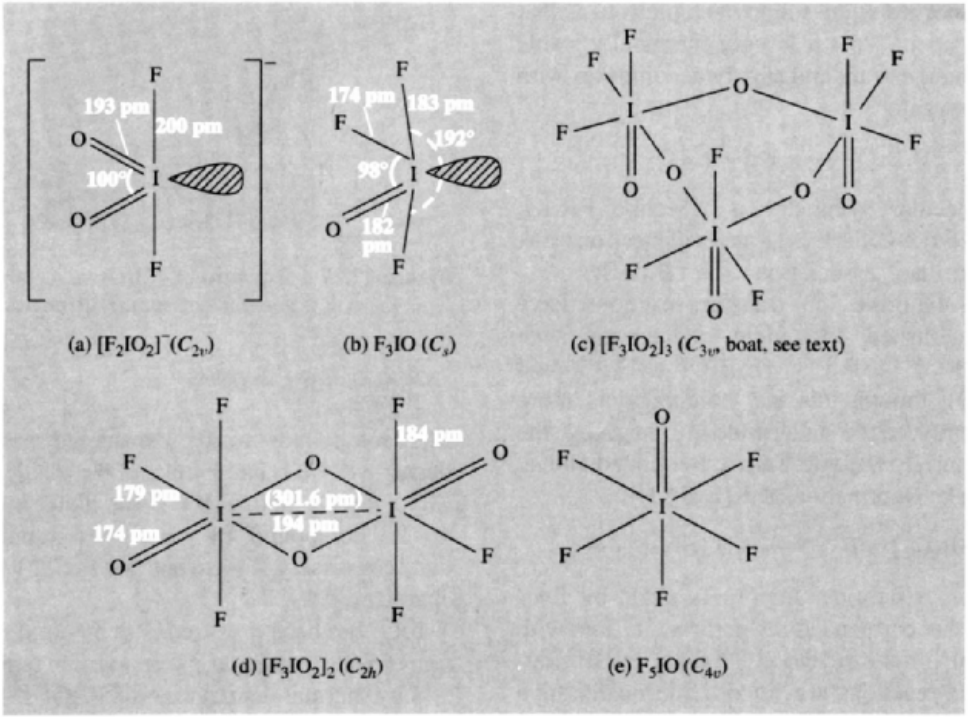


Figure 17.28 Structures of iodine oxide fluorides.

Above 110° it dismutates into FIO_2 and IF_5 as mentioned above.

Of the I^{VII} oxide fluorides FIO_3 has been prepared by the action of F_2/liquid HF on HIO_4. It is a white, crystalline solid, stable in glass but decomposing with loss of oxygen on being heated:

$$FIO_3 \xrightarrow{100^\circ} FIO_2 + \tfrac{1}{2}O_2$$

Unlike its analogue $FClO_3$ it forms adducts with BF_3 and AsF_5, possibly by F^- donation to give $[IO_3]^+[BF_4^-]$ and $[IO_3]^+[AsF_6]^-$, though the structures have not yet been determined. Alternatively, the coordination number of the central I atom might be increased. SO_3 reduces FIO_3 to iodyl fluorosulfate:

$$FIO_3 + SO_3 \longrightarrow IO_2SO_2F + O_2$$

Like $FClO_3$ it reacts with NH_3 but the products have not been fully characterized.

F_3IO_2, first made in 1969, has posed an interesting structural problem. The yellow solid, mp 41°, can be prepared by partial fluorination of a periodate with fluorosulfuric acid:

$$Ba_3H_4(IO_6)_2 \xrightarrow{HSO_3F} [HIO_2F_4] \xrightarrow{SO_3} F_3IO_2$$

Unlike monomeric F_3ClO_2 (p. 878) the structure is oligomeric not only in the solid state but also in the gaseous and solution phases. This arises from the familiar tendency of iodine to increase its coordination number to 6. Fluorine-19 nmr and Raman spectroscopy of F_3IO_2 dissolved in BrF_3 at −48° have been interpreted in terms of a *cis*-oxygen-bridged trimer with axial terminal O atoms and a C_{3v} boat conformation (Fig. 17.28c).[150] On warming the solution to 50° there is a fast interconversion between this and the C_s chair conformer. The vibration spectrum of the gas phase at room temperature has been interpreted in terms of a centrosymmetric dimer

[150] R. J. Gillespie and J. P. Krasznai, *Inorg. Chem.* **15**, 1251–6 (1976).

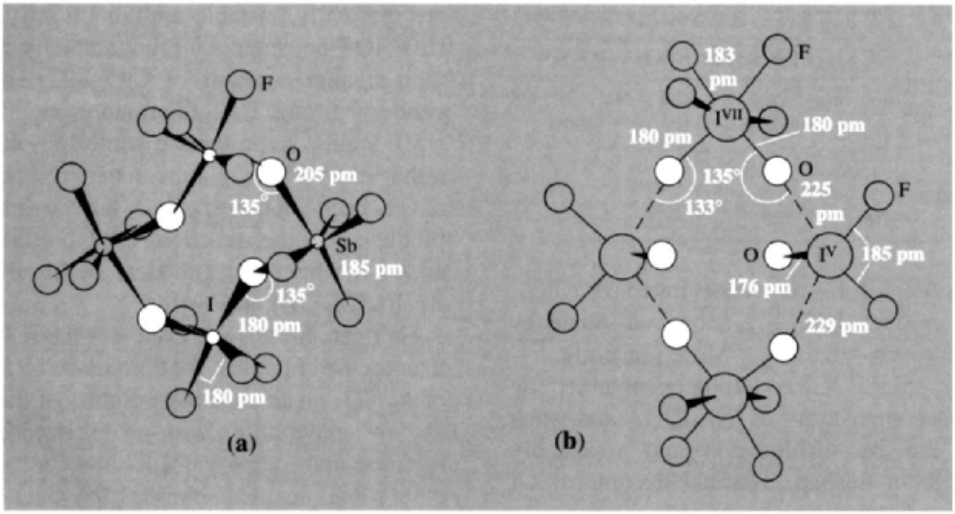


Figure 17.29 Structures of dimeric adducts of F_3IO_2.

(Fig. 17.28d). There is significant dissociation into monomers at 100° and this is almost complete at 185°. The centrosymmetric dimer has also been found in an X-ray study of the crystalline solid at −80° (Fig. 17.28d).[151] Complexes of F_3IO_2 with AsF_5, SbF_5, NbF_5 and TaF_5 have been studied:[152] they are oxygen-bridged polymers with alternating $\{F_4IO_2\}$ and $\{O_2MF_4\}$ groups. For example, the crystal structure of the complex with SbF_5 shows it to be dimeric (Fig. 17.29a).[153] A similar structure motif is found in the adduct $F_3IO.F_3IO_2$ which features alternating 5- and 6-coordinate I atoms (Fig. 17.29b);[154] the structure can be regarded as a cyclic dimer of the ion pair $[F_2IO]^+[F_4IO_2]^-$. See also p. 885 for the mixed valence oxo-iodine polymeric cation in $[(IO_2)_3]^+HSO_4^-$.

Finally in this section we mention iodine oxide pentafluoride, F_5IO, obtained as a colourless liquid, mp 45°, when IF_7 is allowed to react with water, silica, glass or I_2O_5. As implied by its preparation from water, F_5IO is not readily hydrolysed. Vibrational spectroscopy and ^{19}F nmr studies point to the 6-coordinate C_{4v} geometry in Fig. 17.28e (i.e. I^{VII}) rather than the alternative 5-coordinate structure $F_4I^{V}OF$. Microwave spectroscopy yields a value of 1.08 D for the molecular dipole moment.

17.2.10 Halogen derivatives of oxoacids

Numerous compounds are known in which the H atom of an oxoacid has been replaced by a halogen atom. Examples are:

halogen(I) perchlorates	$XOClO_3$ (X=F, Cl, Br, ?I)
halogen(I) fluorosulfates	$XOSO_2F$ (X=F, Cl, Br, I)
halogen(I) nitrates	$XONO_2$ (X=F, Cl, Br, I)

In addition, halogen(III) derivatives such as $Br(ONO_2)_3$, $I(ONO_2)_3$, $Br(OSO_2F)_3$ and $I(OSO_2F)_3$ are known, as well as complexes $M^I[X^I(ONO_2)_2]$, $M^I[I^{III}(ONO_2)_4]$, $M^I[X^{III}(OSO_2F)_4]$ (X=Br, I). In general, thermal stability decreases with increase in atomic number of the halogen.

The properties of halogen(I) perchlorates are in Table 17.25. $FOClO_3$ was originally prepared

[151] L. E. SMART, *J. Chem. Soc., Chem. Commun.*, 519–20 (1977).
[152] R. J. GILLESPIE and J. P. KRASZNAI, *Inorg. Chem.* **16**, 1384–92 (1977).
[153] A. J. EDWARDS and A. A. K. HANA, *J. Chem. Soc., Dalton Trans.*, 1734–6 (1980).
[154] R. J. GILLESPIE, J. P. KRASZNAI and D. R. SLIM, *J. Chem. Soc., Dalton Trans.*, 481–3 (1980).

Table 17.25 Properties of halogen(I) perchlorates

Property	$FOClO_3$	$ClOClO_3$	$BrOClO_3$	$IOClO_3$
Colour	Colourless	Pale yellow	Red	Not obtained pure
MP/°C	−167.3	−117	< −78	
BP/°C	−15.9	44.5	—	
Decomp temp /°C	~100	20	−20	

by the action of F_2 on concentrated $HOClO_3$, but the product had a pronounced tendency to explode on freezing. More recently,[155] extremely pure $FOClO_3$ has been obtained by thermal decomposition of NF_4ClO_4 and such samples can be manipulated and repeatedly frozen without mishap. Thermal decomposition occurs via two routes:

$$ClF + 2O_2 \leftarrow FOClO_3 \rightarrow FClO_2 + O_2$$

It readily oxidizes iodide ions: $FOClO_3 + 2I^- \longrightarrow ClO_4^- + F^- + I_2$. $FOClO_3$ also adds to C=C double bonds in fluorocarbons to give perfluoroalkyl perchlorates:

$$CF_2{=}CF_2 + FOClO_3 \xrightarrow{-45°} CF_3CF_2OClO_3$$

$$CF_3CF{=}CF_2 + FOCl_3 \xrightarrow{-45°} \underset{68\%}{CF_3CF_2CF_2OClO_3} + \underset{32\%}{CF_3CF(OClO_3)CF_3}$$

The formation of isomers in this last reaction implies a low bond polarity of FO– in $FOClO_3$.

Chlorine perchlorate, $ClOClO_3$, is made by low-temperature metathesis:

$$MClO_4 + ClOSO_2F \xrightarrow{-45°} ClOClO_3 + MSO_3F \quad (M{=}Cs, NO_2)$$

The bromine analogue can be made similarly using $BrOSO_2F$ at −20° or by direct bromination of $ClOClO_3$ with Br_2 at −45°. Both compounds are thermally unstable and shock sensitive; e.g. $ClOClO_3$ decomposes predominantly to Cl_2O_6 with smaller amounts of ClO_2, Cl_2 and O_2 on gentle warming. Direct iodination of $ClOClO_3$ at −50° yields the polymeric white solid $I(OClO_3)_3$ rather than $IOClO_3$; this latter compound has never been obtained pure but is among the products of the reaction of I_2 with $AgClO_4$ at −85°, the other products being $I(OClO_3)_3$, $Ag[I(OClO_3)_2)]$ and AgI.

Halogen nitrates are even less thermally stable than the perchlorates: they are made by the action of $AgNO_3$ on an alcoholic solution of the halogen at low temperature. With an excess of $AgNO_3$, bromine and iodine yield $X(ONO_2)_3$. Numerous other routes are available; e.g., the reaction of ClF on $HONO_2$ gives a 90% yield of $ClONO_2$ and the best preparation of this compound is probably the reaction

$$Cl_2O + N_2O_5 \xrightarrow{0°} 2ClONO_2$$

Some physical properties are in Table 17.26. Both $FONO_2$ and $ClONO_2$ feature planar NO_3 groups with the halogen atom out of the plane. $ClONO_2$ has been used to convert metal chlorides to anhydrous metal nitrates, e.g. $Ti(NO_3)_4$. Likewise ICl_3 at −30° yields $I(ONO_2)_3$. $ClONO_2$ and $IONO_2$ add across C=C double bonds, e.g.:

$$CH_2{=}CMe_2 + Cl{-}ONO_2 \xrightarrow{-78°} ClCH_2C(Me_2)ONO_2$$

Table 17.26 Some properties of halogen(I) nitrates

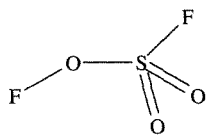
Property	$FONO_2$	$ClONO_2$	$BrONO_2$	$IONO_2$
Colour	Colourless	Colourless	Yellow	Yellow
MP/°C	−175	−107	−42	—
BP/°C	−45.9	18	—	—
Decomp temp/°C	Ambient	Ambient	<0	<0
$\Delta H_f^\circ(g, 298\ K)$/ kJ mol^{-1}	+10.5	+29.2	—	—
$\Delta G_f^\circ(g, 298\ K)$/ kJ mol^{-1}	+73.5	+92.4	—	—

Several other reactions have been studied but the overall picture is one of thermal instability,

[155] C. J. SCHACK and K. O. CHRISTE, *Inorg. Chem.* **18**, 2619–20 (1979). For vibrational spectra, thermodynamic properties and confirmation of C_s structure see K. O. CHRISTE and E. C. CURTIS, *Inorg. Chem.* **21**, 2938–45 (1982).

hazardous explosions, and vigorous chemical reactivity leading to complex mixtures of products.

The halogen fluorosulfates are amongst the most stable of the oxoacid derivatives of the halogens. $FOSO_2F$ is made by direct addition of F_2 to SO_3 and the others are made by direct combination of the halogen with an equimolar quantity of peroxodisulfuryl difluoride, $S_2O_6F_2$ (p. 640). With an excess of $S_2O_6F_2$, bromine and iodine yield $X(OSO_2F)_3$. An alternative route to $ClOSO_2F$ is the direct addition of ClF to SO_3, whilst $BrOSO_2F$ and $IOSO_2F$ can be made by thermal decomposition of the corresponding $X(OSO_2F)_3$. The halogen fluorosulfates are thermally unstable, moisture sensitive, highly reactive compounds. Some physical properties are summarized in Table 17.27. The vibrational spectra of $FOSO_2$ and $ClOSO_2F$ are consistent with C_s molecular symmetry as in $HOSO_2F$:



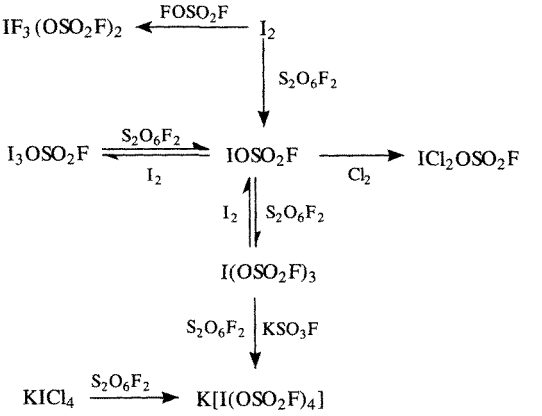
Much of the chemistry of the halogen fluorosulfates resembles that of the interhalogens (p. 824) and in many respects the fluorosulfate group can be regarded as a pseudohalogen (p. 319). There is some evidence of ionic self-dissociation and reactions can be classified as exchange, addition, displacement and complexation. This is illustrated for the iodine fluorosulfates in the following scheme:[156]

Table 17.27 Some physical properties of halogen fluorosulfates[a]

Property	$FOSO_2F$	$ClOSO_2F$	$BrOSO_2F$	$IOSO_2F$
Colour	Colourless	Yellow	Red-brown	Black
State at room temp	Gas	Liquid	Liquid	Solid
MP/°C	−158.5	−84.3	−31.5	51.5
BP/°C	−31.3	45.1	117.3	—

[a] $Br(OSO_2F)_3$ is a pale yellow solid, mp 59°; $I(OSO_2F)_3$ is a pale yellow solid, mp 32°.

[156] Ref. 23, pp. 1466–75, Halogen derivatives of oxyacids.



$BrOSO_2F$ has also been used to prepare new *N*-bromo sulfonimides such as $(CF_3SO_2)_2NBr$.[157] Other novel compounds include $[I(OSO_2F)_2]^+$-I^-[158] and the mixed valent iodine (III,V) polycation in $[(IO_2)_3]^+HSO_4^-$.[159]

17.3 The Chemistry of Astatine[160,161]

All isotopes of element 85, astatine, are intensely radioactive with very short half-lives (p. 795). As a consequence weighable amounts of the element or its compounds cannot be prepared and no bulk properties are known. The chemistry of the element must, of necessity, be studied by tracer techniques on extremely dilute solutions, and this introduces the risk of experimental errors and the consequent possibility of erroneous

[157] S. SINGH and D. D. DESMARTEAU, *Inorg. Chem.* **25**, 4596–7 (1986).

[158] M. J. COLLINS, G. DÉNÈS and R. J. GILLESPIE, *J. Chem. Soc., Chem. Commun.*, 1296–7 (1984).

[159] A. REHR and M. JANSEN, *Z. anorg. allg. Chem.* **608**, 159–65 (1992).

[160] E. H. APPELMAN, Astatine, Chap. 6 in *MTP International Review of Science, Inorganic Chemistry*, Series 1. Vol. 3, *Main Group Elements Group VII and Noble Gases*, pp. 181–98, Butterworths, London, 1972; see also ref. 23, pp. 1573–94, Astatine.

[161] T. J. RUTH, M. DOMBSKY, J. M. D'AURIA and T. E. WARD, *Radiochemistry of Astatine*, US Dept. of Energy, Nuclear Science Series NAS-NS-3064 (DE 880 15386), Washington, DC, 1988, 80 pp.

conclusions. Nevertheless, a picture of the element is emerging, as outlined below. The synthesis of the element (p. 795), its natural occurrence in rare branches of the ^{235}U decay series (p. 796), and its atomic properties (p. 800) have already been mentioned.

The chemistry of At is most conveniently studied using ^{211}At ($t_{\frac{1}{2}}$ 7.21 h). This isotope is prepared by α-particle bombardment of ^{209}Bi using acceleration energies in the range 26–29 MeV. Higher energies result in the concurrent formation of ^{210}At and ^{209}At which complicate the subsequent radiochemical assays. The Bi is irradiated either as the metal or its oxide and the target must be cooled to avoid volatilization of the At produced. Astatine is then removed by heating the target to 300–600° (i.e. above the mp of Bi, 217°) in a stream of N_2 and depositing the sublimed element on a glass cold finger or cooled Pt disc. Aqueous solutions of the element can be prepared by washing the cold finger or disc with dilute HNO_3 or HCl. Alternatively, the irradiated target can be dissolved in perchloric acid containing a little iodine as carrier for the astatine; the Bi is precipitated as phosphate and the aqueous solution of AtI used as it is or the activity can be extracted into CCl_4 or $CHCl_3$.

Five oxidation states of At have been definitely established (–I, 0, +I, V, VII) and one other (III) has been postulated. The standard oxidation potentials connecting these states in 0.1 M acid solution are $E°$/V):

$$At^- \xleftarrow{+0.3} At(0) \xleftarrow{+1.0} HOAt \xleftarrow{+1.5} AtO_3^- \xleftarrow{>+1.6} AtO_4^-$$

These values should be compared with those for the other halogens (in 1 M acid) (p. 854). Noteworthy features are that At is the only halogen with an oxidation state between 0 and V that is thermodynamically stable towards disproportionation, and that the smooth trends in the values of $E°(\frac{1}{2}X_2/X^-)$ and $E°(HOX/\frac{1}{2}X_2)$ continue to At.

The astatide ion At^- (which coprecipitates with AgI, TlI, PtI_2 or PdI_2) can be obtained from At(0) or AtI using moderately powerful reducing agents, e.g. Zn/H^+, SO_2, SO_3^{2-}/OH^-, $[Fe(CN)_6]^{4-}$ or As^{III}. Reoxidation to At(0) can be effected by the weak oxidants $[Fe(CN)_6]^{3-}$, As^V or dilute HNO_3. Oxidants of intermediate power (e.g. Cl_2, Br_2, Fe^{3+}, $Cr_2O_7^{2-}$, VO^{2+}) convert astatine to an intermediate oxidation state which is most probably AtO^- or At^+ and which does not extract into CCl_4. Powerful oxidants (Ce^{IV}, $NaBiO_3$, $S_2O_8^{2-}$, IO_4^-) convert At(0) directly to AtO_3^- (carried by $AgIO_3$, $Ba(IO_3)_2$, etc., and not extractable into CCl_4). The perastatate ion, AtO_4^-, was first conclusively prepared by V. A. Khalkin's group in the USSR in 1970 using solid XeF_2 in hot NaOH solution at pH ~ 10. It is unstable in acid solutions, being completely decomposed to AtO_3^- within 5–10 minutes at pH 1 and 90°C, for example.

At(0) reacts with halogens X_2 to produce interhalogen species AtX, which can be extracted into CCl_4, whereas halide ions X^- yield polyhalide ions AtX_2^- which are not extracted by CCl_4 but can be extracted into Pr^i_2O. The equilibrium formation constants of the various trihalide ions are intercompared in Table 17.28.

A rudimentary chemistry of organic derivatives of astatine is emerging, but the problems of radiation damage, product separation and tracer

Table 17.28 Formation constants for trihalide ions at 25°C

Reaction	K/l mol^{-1}	Reaction	K/l mol^{-1}
$Cl_2 + Cl^- \rightleftharpoons Cl_3^-$	0.12	**$AtI + Br^- \rightleftharpoons AtIBr^-$**	**120**
$Br_2 + Cl^- \rightleftharpoons Br_2Cl^-$	1.4	$ICl + Cl^- \rightleftharpoons ICl_2^-$	170
$I_2 + Cl^- \rightleftharpoons I_2Cl^-$	3	**$AtBr + Br^- \rightleftharpoons AtBr_2^-$**	**320**
$AtI + Cl^- \rightleftharpoons AtICl^-$	**9**	$IBr + Br^- \rightleftharpoons IBr_2^-$	440
$Br_2 + Br^- \rightleftharpoons Br_3^-$	17	$I_2 + I^- \rightleftharpoons I_3^-$	800
$IBr + Cl^- \rightleftharpoons IBrCl^-$	43	**$AtI + I^- \rightleftharpoons AtI_2^-$**	**2000**

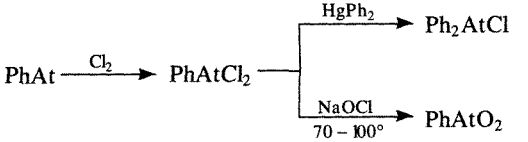
identification, already severe for inorganic compounds of astatine, are even worse with organic derivatives. Two reviews are available.[162,163] Various compounds of the type RAt, $RAtCl_2$, R_2AtCl and $RAtO_2$ (R = phenyl or *p*-tolyl) have been synthesized using astatine-labelled iodine reagents, e.g.:

$$Ph_2I.I \xrightarrow{At^-} Ph_2IAt \xrightarrow{175°} PhI + PhAt$$

$$PhI \xrightarrow{AtI} PhAt$$

$$PhI \xrightarrow[130-200°]{At^-} PhAt$$

$$PhN_2Cl \xrightarrow{At^-} PhAt$$



In addition, demercuriation reactions have resulted in a wide variety of rather complex compounds including aromatic aminoacids, steroids, imidazols, etc. in good yields (at the tracer level). The driving force in these studies has been the hope of incorporating ^{211}At into biologically active compounds for therapautic use.

Astatine has been shown to be superior to radio-iodine for the destruction of abnormal thyroid tissue (p. 794) because of the localized action of the emitted α-particles which dissipate 5.9 MeV within a range of 70 μm of tissue, whereas the much less energetic β-rays of radio-iodine have a maximum range of *ca.* 2000 μm. However, its general inaccessibility and high cost render its extensive application unlikely.

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[162] K. BEREI and L. VASAROS, The Organic Chemistry of Astatine, in S. PATAI and Z. RAPPAPORT (eds.), *The Chemistry of Organic Functional Groups*, Wiley, New York, 1983.

[163] H. H. COENEN, S. M. MOERLEIN and G. STÖCKLIN, *Radiochem. Acta* **34**, 47–68 (1983).