

anions IBr_2^- and I_3^- the salts become ambient pressure superconductors.⁽⁸³⁾

17.2.5 Polyhalonium cations XY_{2n}^+

Numerous polyhalonium cations have already been mentioned in Section 17.2.3 during the discussion of the self-ionization of interhalogen compounds and their ability to act as halide-ion donors. The known species are summarized in Table 17.16.^(84,85) Preparations are usually by addition of the appropriate interhalogen and halide-ion acceptor, or by straightforward modification of this general procedure in which the interhalogen or halogen is also used as an oxidant. For example Au dissolves in BrF_3 to give $[BrF_2][AuF_4]$, BrF_3 fluorinates and oxidizes $PdCl_2$ and $PdBr_2$ to $[BrF_2][PdF_4]$; ClF_3 converts

$AsCl_3$ to $[ClF_2][AsF_6]$; stoichiometric amounts of I_2 , Cl_2 and $2SbCl_5$ yield $[ICl_2][SbCl_6]$. The fluorocations tend to be colourless or pale yellow but the colour deepens with increasing atomic weight so that compounds of ICl_2^+ are wine-red or bright orange whilst I_2Cl^+ compounds are dark brown or purplish black.

Structures are as expected from simple valency theory and the isoelectronic principle (20 valency electrons). Thus the triatomic species are bent, rather than linear, as illustrated in Fig. 17.13 for ClF_2^+ , BrF_2^+ and ICl_2^+ ; there is frequently some residual interionic interaction due to close approach of the cation and anion and this sometimes complicates the interpretation of vibrational spectroscopic data. In the case of $[ICl_2][SbF_6]$ (Fig. 17.13c) the very short $I \cdots F$ distance implies one of the strongest secondary interactions known between these two elements and the $Sb-F \cdots I$ angle deviates appreciably from linearity.⁽⁸⁶⁾ The ion $[Cl_2F]^+$ was originally thought to have the symmetrical

⁸³ T. J. EMGE and 12 others, *J. Am. Chem. Soc.* **108**, 695–702 (1986).

⁸⁴ J. SHAMIR, *Struct. Bonding* **37**, 141–210 (1979).

⁸⁵ T. BIRCHALL and R. D. MEYERS, *Inorg. Chem.* **21**, 213–7 (1982).

⁸⁶ T. BIRCHALL and R. D. MEYERS, *Inorg. Chem.* **20**, 2207–10 (1981).

Table 17.16 Polyhalonium cations, XY_{2n}^+

Cation	(Date) ^(a)	Examples of co-anions (mp of compound in parentheses)
ClF_2^+	(1950)	BF_4^- (30°), PF_6^- , AsF_6^- , SbF_6^- (78°), PtF_6^- (171°), SnF_6^{2-}
Cl_2F^+	(1969)	BF_4^- , AsF_6^-
BrF_2^+	(1949)	PdF_4^- , AuF_4^- , AsF_6^- , SbF_6^- (130°), $Sb_2F_{11}^-$ (33.5°), BiF_6^- , NbF_6^- , TaF_6^- , GeF_6^{2-} (subl 20°), SnF_6^{2-} , PtF_6^{2-} (136°), SO_3F^-
IF_2^+	(1968)	BF_4^- , AsF_6^- (d – 22°), SbF_6^- (d 45°)
ICl_2^+	(1959)	$AlCl_4^-$ (105°), $SbCl_6^-$ (83.5°), $Sb_2F_{11}^-$ (62°), SO_3F^- (42°), SO_3Cl^- (8°)
I_2Cl^+	(1972)	$AlCl_4^-$ (53°), $SbCl_6^-$ (70°), $TaCl_6^-$ (102°), SO_3F^- (40°)
IBr_2^+	(1971)	$Sb_2F_{11}^-$ (65°), SO_3F^- (97°), $SO_3CF_3^-$ (75°)
I_2Br^+	(1974)	SO_3F^- (70°)
$IBrCl^+$	(1973)	$SbCl_6^-$, SO_3F^- (65°)
ClF_4^+	(1967)	AsF_6^- , SbF_6^- (88°), $Sb_2F_{11}^-$ (64°), PtF_6^-
BrF_4^+	(1957)	AsF_6^- , $Sb_2F_{11}^-$ (60°), SnF_6^{2-}
IF_4^+	(1950)	SbF_6^- (103°), $Sb_2F_{11}^-$, PtF_6^- , SO_3F^- , SnF_6^{2-}
$I_3Cl_2^+$	(1982)	$SbCl_6^-$ (47°)
ClF_6^+	(1972)	PtF_6^- (d140°)
BrF_6^+	(1973)	AsF_6^- , $Sb_2F_{11}^-$
IF_6^+	(1958)	BF_4^- , AsF_6^- (subl 120°), SbF_6^- (175°), $Sb_2F_{11}^-$, $[(SbF_5)_3F]^-$ (94°), AuF_6^-

^(a)The date given refers to the first isolation of a compound containing the cation, or the characterization of the cation in solution.

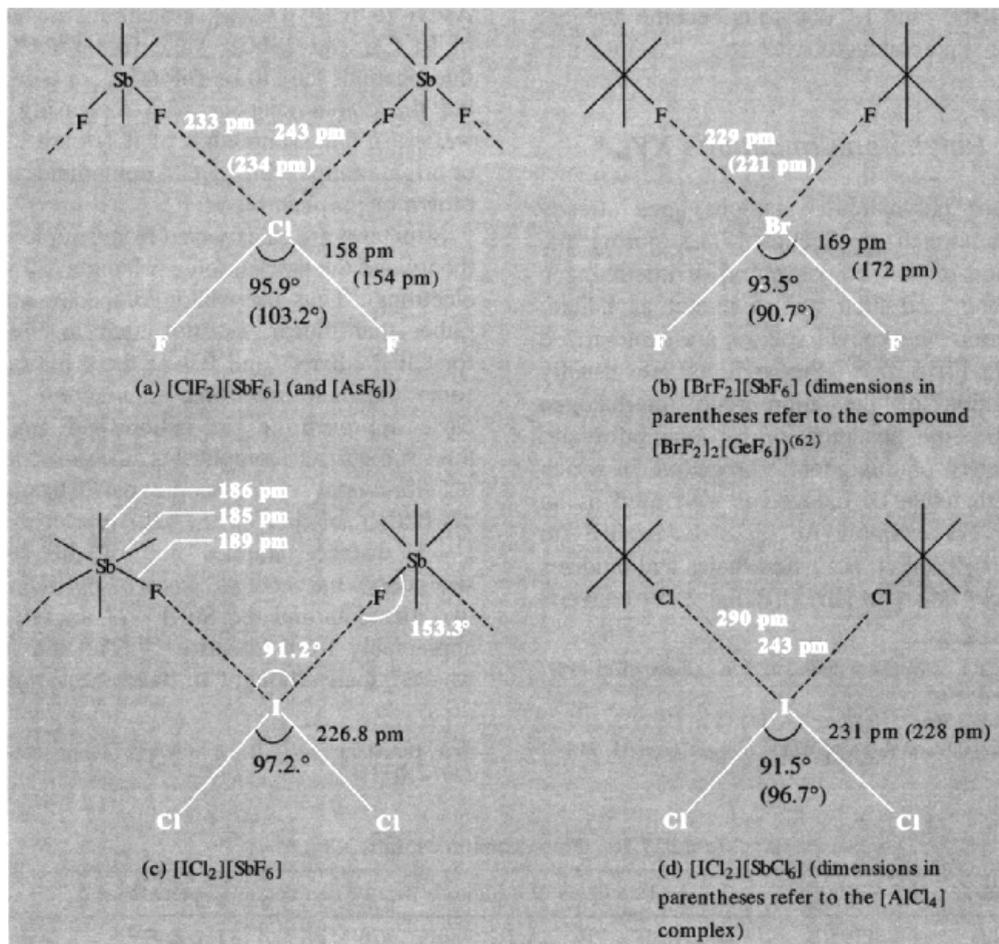
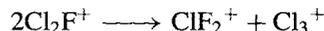


Figure 17.13 Chain structures of compounds containing the triatomic cations XY_2^+ : (a) $[\text{ClF}_2][\text{SbF}_6]$ (with dimensions for $[\text{ClF}_2][\text{AsF}_6]$ in parentheses); (b) $[\text{BrF}_2][\text{SbF}_6]$; (c) $[\text{ICl}_2][\text{SbF}_6]$ indicating slightly bent $\text{Sb}-\text{F}\cdots\text{I}$ configuration and very short $\text{I}\cdots\text{F}$ distance; and (d) $[\text{ICl}_2][\text{SbCl}_6]$ (with dimensions for the $[\text{AlCl}_4]^-$ salt in parentheses).

bent C_{2v} structure $[\text{Cl}-\text{F}-\text{Cl}]^+$ but later Raman spectroscopic studies were interpreted on the basis of the unsymmetrical bent structure $[\text{Cl}-\text{Cl}-\text{F}]^+$. Calculations⁽⁸⁷⁾ suggest that the symmetrical C_{2v} structure is indeed the more stable form at least for the isolated cation and the question must be regarded as still open:

it may well be that the configuration adopted is determined by residual interactions in the solid state or in solution. In fact the ion is rather unstable in solution and disproportionates completely in SbF_5/HF even at -76° :



The pentaatomic cations ClF_4^+ , BrF_4^+ and IF_4^+ are precisely isoelectronic with SF_4 , SeF_4 and TeF_4 and adopt the same T-shaped (C_{2v}) configuration. This is illustrated in Fig. 17.14

⁸⁷ B. D. JOSHI and K. MOROKUMA, *J. Am. Chem. Soc.* **101**, 1714-7 (1979), and references therein.

⁸⁸ A. J. EDWARDS and K. G. CHRISTE, *J. Chem. Soc., Dalton Trans.*, 175-7 (1976)

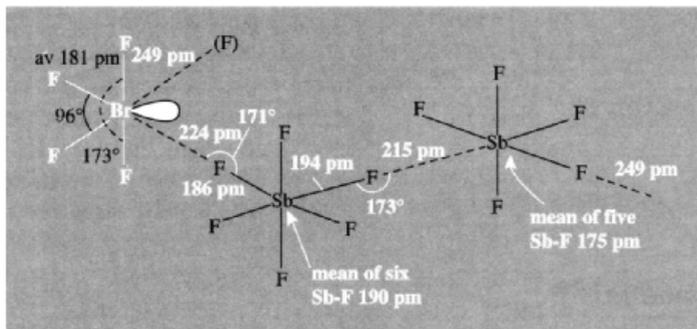
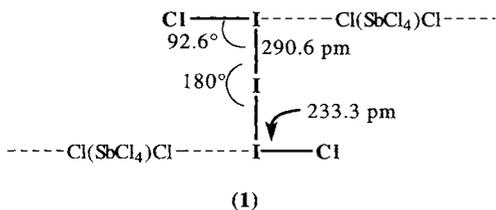


Figure 17.14 Structure of $[\text{BrF}_4][\text{Sb}_2\text{F}_{11}]$ (see text).

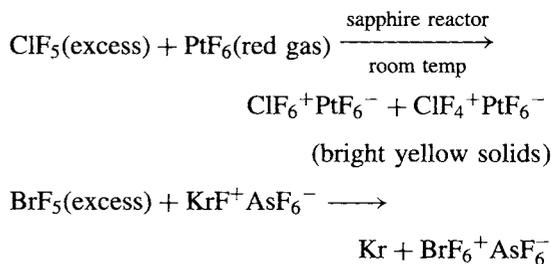
for the case of $[\text{BrF}_4][\text{Sb}_2\text{F}_{11}]$: again there are strong subsidiary interactions, the coordination about Br being pseudooctahedral with four short Br-F distances and two longer Br...F distances which are no doubt influenced by the presence of the stereochemically active nonbonding pair of electrons on the Br atom. In addition, the mean Sb-F distance in the central SbF_6 unit is substantially longer than the mean of the five "terminal" Sb-F distances in the second unit and the structure can be described approximately as $[\text{BrF}_4^+ \cdots \text{SbF}_6^- \cdots \text{SbF}_5]$. The structure of the final pentaatomic cation, I_3Cl_2^+ (1), is different and resembles that of I_5^+ (p. 844) in being a planar centrosymmetric species with C_{2h} symmetry:⁽⁸⁵⁾



It will be noted that the central I-I distance is close to that in I_5^+ and that the terminal I-Cl distance is very similar to that in $\beta\text{-ICl}$ (p. 826). There are also strong secondary interactions so as to form infinite zig-zag chains via *trans*-Cl atoms of the octahedral SbCl_6^- anions ($\text{I} \cdots \text{Cl}$ 294.1 pm, angle $\text{Cl}-\text{I} \cdots \text{I}$ 177.6°).

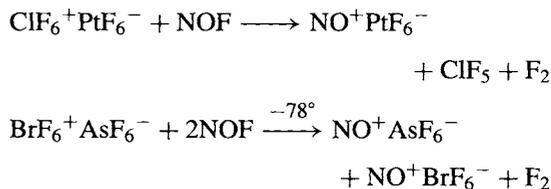
Of the heptaatomic cations, IF_6^+ has been known for some time since it can be made

by fluoride-ion transfer from IF_7 . Because ClF_7 and BrF_7 do not exist, alternative preparative procedures must be devised and compounds of ClF_6^+ and BrF_6^+ are of more recent vintage (Table 17.16). The cations have been made by oxidation of the pentafluorides with extremely strong oxidizers such as PtF_6 , KrF^+ , or KrF_3^+ , e.g.:⁽⁸⁴⁾

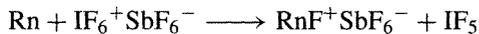
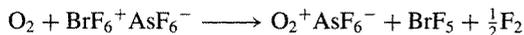


Vibrational spectra and ^{19}F nmr studies on all three cations XF_6^+ and the ^{129}I Mössbauer spectrum of $[\text{IF}_6][\text{AsF}_6]$ establish octahedral (O_h) symmetry as expected for species isoelectronic with SF_6 , SeF_6 and TeF_6 respectively.

Attempts to prepare ClF_7 and BrF_7 by reacting the appropriate cation with NOF failed; instead the following reactions occurred:



As expected, the cations are extremely powerful oxidants, e.g.:



17.2.6 Halogen cations^(84,89)

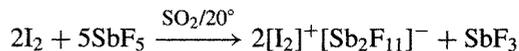
It has been known for many years that iodine dissolves in strongly oxidizing solvents such as oleum to give bright blue paramagnetic solutions, but only in 1966 was this behaviour unambiguously shown to be due to the formation of the diiodine cation I_2^+ . (The production of similar brightly coloured solutions of S, Se and Te has already been discussed on pp. 664, 759.) The ionization energies of Br_2 and Cl_2 , whilst greater than that for I_2 (Table 17.17), are nevertheless smaller than for O_2 , which can likewise be oxidized to O_2^+ (p. 616). Accordingly, compounds of the bright-red cationic species Br_2^+ are now well established, but Cl_2^+ is known only from its electronic band spectrum obtained in a low-pressure discharge tube. Some properties of the three diatomic cations X_2^+ are compared with those of the parent halogen molecules X_2 in Table 17.17; as expected, ionization reduces the interatomic distance and increases the vibration frequency ($\nu \text{ cm}^{-1}$) and

Table 17.17 Comparison of diatomic halogens X_2 and their cations X_2^+

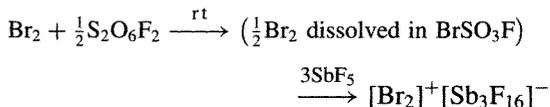
Species	$I/\text{kJ mol}^{-1}$	r/pm	ν/cm^{-1}	$k/\text{N m}^{-1(a)}$	$\lambda_{\text{max}}/\text{nm}$
Cl_2	1110	199	554	316	330
Cl_2^+	—	189	645	429	—
Br_2	1014	228	319	238	410
Br_2^+	—	213	360	305	510
I_2	900	267	215	170	520
I_2^+	—	256	238	212	640

^(a)Force constant k in newton/metre: 1 millidyne/Å = 100 N m⁻¹.

force constant ($k \text{ N m}^{-1}$). The principal synthetic routes to crystalline compounds of Br_2^+ and I_2^+ have been either (a) the comproportionation of BrF_3 , BrF_5 or IF_5 with the stoichiometric amount of halogen in the presence of SbF_5 , or (b) the direct oxidation of the halogen by an excess of SbF_5 or by SbF_5 dissolved in SO_2 , e.g.:

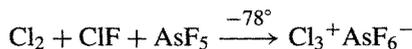


More recently⁽⁹⁰⁾ a simpler route has been devised which involves oxidation of Br_2 or I_2 with the peroxide $\text{S}_2\text{O}_6\text{F}_2$ (p. 640) followed by solvolysis using an excess of SbF_5 , e.g.:



The bright-red crystals of $[\text{Br}_2]^+[\text{Sb}_3\text{F}_{16}]^-$ melt at 85.5°C to a cherry-red liquid. Dark-blue crystals of $[\text{I}_2]^+[\text{Sb}_2\text{F}_{11}]^-$ melt sharply at 127°C and the corresponding blue solid $[\text{I}_2]^+[\text{Ta}_2\text{F}_{11}]^-$ melts at 120°C. When solutions of I_2^+ in HSO_3F are cooled below -60°C there is a dramatic colour change from deep blue to red as the cation dimerizes: $2\text{I}_2^+ \rightleftharpoons \text{I}_4^{2+}$. There is a simultaneous drop in the paramagnetic susceptibility of the solution and in its electrical conductivity. The changes are rapid and reversible, the blue colour appearing again on warming.

During the past 20 y numerous other highly coloured halogen cations have been characterized by Raman spectroscopy, X-ray crystallography, and other techniques, as summarized in Table 17.18. Typical preparative routes involve direct oxidation of the halogen (a) in the absence of solvent, (b) in a solvent which is itself the oxidant (e.g. AsF_5) or (c) in a non-reactive solvent (e.g. SO_2). Some examples are listed below:



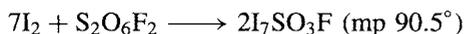
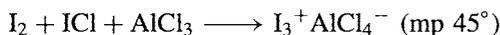
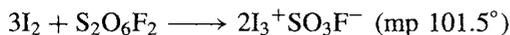
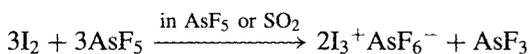
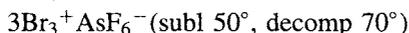
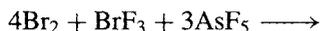
⁸⁹ R. J. GILLESPIE and J. PASSMORE *Adv. Inorg. Chem. Radiochem.* **17**, 49–87 (1975).

⁹⁰ W. W. WILSON, R. C. THOMPSON and F. AUBKE, *Inorg. Chem.* **19**, 1489–93 (1980).

Table 17.18 Summary of known halogen cations

(Cl ₂ ⁺)	Br ₂ ⁺ cherry red	I ₃ ⁺ bright blue
Cl ₃ ⁺ yellow	Br ₃ ⁺ brown	I ₃ ⁺ dark brown/black
	—	I ₄ ²⁺ red-brown
	Br ₅ ⁺ dark brown	I ₅ ⁺ green/black ^(a)
	—	(I ₇ ⁺) black

^(a)[I₅][AlCl₄] is described as greenish-black needles, dark brown-red in thin sections.



Other compounds that have been prepared⁽⁹¹⁾ include the dark-brown gold(III) complexes

⁹¹ K. C. LEE and F. AUBKE, *Inorg. Chem.* **19**, 119–22 (1980).

Br₃[Au(SO₃F)₄] (decomp ~150°C) and Br₅[Au(SO₃F)₄] (mp 65°).

The triatomic cations X₃⁺ are nonlinear and thus isostructural with other 20-electron species such as XY₂⁺ (p. 839) and SCl₂ (p. 689). The contrast in bond lengths and angles between I₃⁺ (Fig. 17.15)⁽⁹²⁾ and the linear 22-electron anion I₃⁻ (p. 836) is notable, as is its similarity with the isoelectronic Te₃²⁻ anion (p. 764). Likewise, Br₃AsF₆ is isomorphous with I₃AsF₆ and the non-linear cation has Br–Br 227.0 pm and an angle of 102.5°⁽⁹³⁾ (cf. Br₃⁻, Table 17.15). The structures of the penta-atomic cations Br₅⁺ (2)⁽⁹⁴⁾ and I₅⁺ (3)⁽⁹⁵⁾ have been determined by X-ray analysis of their AsF₆⁻ salts and shown to have centrosymmetric C_{2h} symmetry like the

⁹² J. PASSMORE, G. SUTHERLAND and P. S. WHITE, *Inorg. Chem.* **20**, 2169–71 (1981).

⁹³ K. O. CHRISTE, R. BAU and D. ZHAO, *Z. anorg. allg. Chem.* **593**, 46–60 (1991).

⁹⁴ H. HARTL, J. NOWICKI and R. MINKWITZ, *Angew. Chem. Int. Edn. Engl.* **30**, 328–9 (1991). See also K. O. CHRISTE, D. A. DIXON and R. MINKWITZ, *Z. anorg. allg. Chem.* **612**, 51–5 (1992).

⁹⁵ A. APBLET, F. GREIN, J. P. JOHNSON, J. PASSMORE and P. S. WHITE, *Inorg. Chem.* **25**, 422–6 (1986).

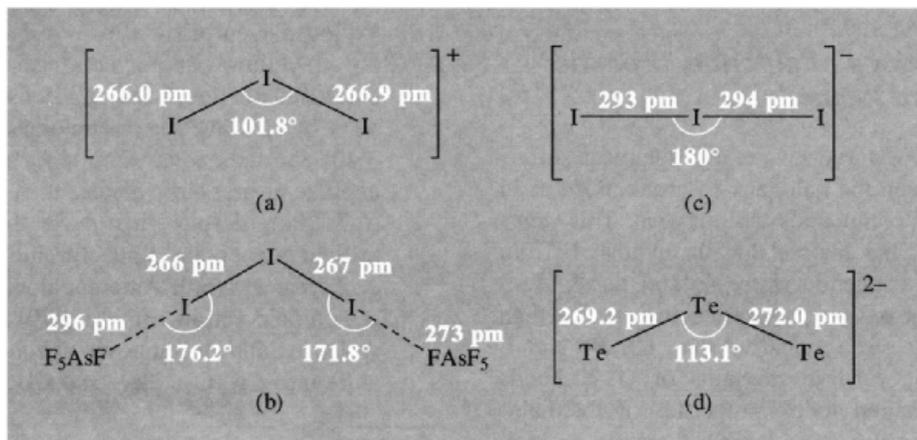
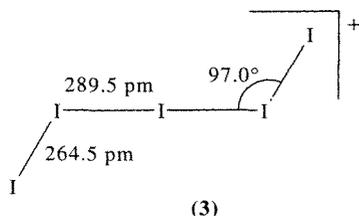
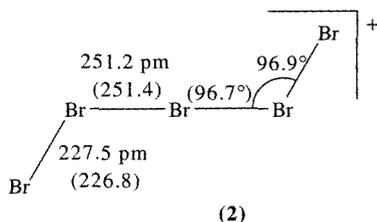


Figure 17.15 The structure of (a) the nonlinear I₃⁺ cation in I₃AsF₆ and (b) the weaker cation–anion interactions along the chain (cf. Fig. 17.13). For comparison, the dimensions of (c) the linear 22-electron cation I₃⁻ and (d) the nonlinear 20-electron cation Te₃²⁻ are given. The data for this latter species refer to the compound [K(crypt)]₂Te₃.en; in K₂Te₃ itself, where there are stronger cation–anion interactions, the dimensions are $r = 280$ pm and angle = 104.4°.

analogous cation $I_3Cl_2^+$ (1) (p. 841). The figures in parenthesis in (2) refer to the SbF_6^- salt.



The black compound I_7SO_3F (mp 90.5°) was established⁽⁹⁶⁾ as a local mp maximum in the phase diagram of the system $I_2/S_2O_6F_2$, together with the known compounds I_3SO_3F (mp 101.5°), ISO_3F (mp 50.2°), and $I(SO_3F)_3$ (mp 33.7°), but its structure has not been determined and there is at present no evidence for the presence of the discrete heptaatomic cation I_7^+ in the crystals.

17.2.7 Oxides of chlorine, bromine and iodine

Perhaps nowhere else are the chemical differences between the halogens so pronounced as in their binary compounds with oxygen. This stems partly from the factors that distinguish F from its heavier congeners (p. 804) and partly from the fact that oxygen is less electronegative than F but more electronegative than Cl, Br and I. The varying relative strengths of O–X bonds and the detailed redox properties of the halogens also ensure considerable diversity in stoichiometry, structure, thermal stability and chemical reactivity of the various species. The binary

compounds between O and F have already been described (p. 638). About 25 further binary halogen oxide species are known, which vary from shock-sensitive liquids and short-lived free radicals to rather stable solids. It will be convenient to treat the 3 halogens separately though intercomparison of corresponding species is instructive and the chemistry is also, at times, related to that of the oxoacids (p. 853) and the halogen oxide fluorides (p. 875).

Oxides of chlorine^(97,98)

Despite their instability (or perhaps because of it) the oxides of chlorine have been much studied and some (such as Cl_2O and particularly ClO_2) find extensive industrial use. They have also assumed considerable importance in studies of the upper atmosphere because of the vulnerability of ozone in the stratosphere to destruction by the photolysis products of chlorofluorocarbons (p. 848). The compounds to be discussed are:

Cl_2O : a brownish-yellow gas at room temperature (or red-brown liquid and solid at lower temperatures) discovered in 1834; it explodes when heated or sparked.

Cl_2O_3 : a dark-brown solid (1967) which explodes even below 0° .

ClO_2 : a yellow paramagnetic gas (deep-red paramagnetic liquid and solid) discovered in 1811 by H. Davy; the liquid explodes above -40° and the gas at room temperature may explode at pressures greater than 50 mmHg (6.7 kPa); despite this more than half a million tonnes are made for industrial use each year in North America alone.

Cl_2O_4 : a pale-yellow liquid (1970), $ClOClO_3$, which readily decomposes at room temperature into Cl_2 , O_2 , ClO_2 and Cl_2O_6 .

⁹⁷ Ref. 23, pp. 1361–86. The oxides of the halogens.

⁹⁸ J. A. WOJCIWICZ, Dichlorine monoxide, hypochlorous acid and hypochlorites. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Wiley, New York, 1993, Vol. 5, pp. 932–68. J. J. KACZUR and D. W. CAWLFIELD, Chlorine dioxide, chlorous acid and chlorites, *ibid.*, pp. 968–91.

⁹⁶ C. CHUNG and G. H. CADY, *Inorg. Chem.* **11**, 2528–31 (1972).

Cl_2O_6 : a dark-red liquid (1843) which is in equilibrium with its monomer ClO_3 in the gas phase; it decomposes to ClO_2 and O_2 .

Cl_2O_7 : a colourless oily liquid (1900) which can be distilled under reduced pressure.

In addition, there are the short-lived radical ClO , the chlorine peroxide radical ClOO (cf. OCIO above), and the tetroxide radical ClO_4 (p. 850).

Some physical and molecular properties are summarized in Table 17.19. All the compounds are endothermic, having large positive enthalpies and free energies of formation. Structural data are in Fig. 17.16. Cl_2O has C_{2v} symmetry, as expected for a molecule with 20 valency-shell electrons; the dimensions indicate normal single bonds, and the bond angle can be compared with those for similar molecules such as OF_2 , H_2O , SCl_2 , etc. Chlorine dioxide, ClO_2 , also has C_{2v} symmetry but there are only 19 valency-shell electrons and this is reflected in the considerable shortening of the $\text{Cl}-\text{O}$ bonds and the increase in the bond angle, which is only 1.7° less than in the 18-electron species SO_2 (p. 700). ClO_2 is an interesting example of an odd-electron molecule which is stable towards dimerization (cf. NO , p. 445); calculations suggest that the odd electron is delocalized throughout the molecule and this probably explains the reluctance to dimerize. Indeed, there is no evidence of dimerization even

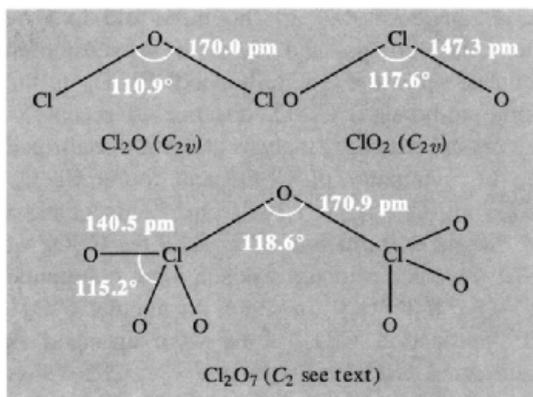


Figure 17.16 Molecular structure and dimensions of gaseous molecules of chlorine oxides as determined by microwave spectroscopy (Cl_2O and ClO_2) or electron diffraction (Cl_2O_7).

in the liquid or solid phases, or in solution. This contrasts with the precisely isoelectronic thionite ion SO_2^- which exists as dithionite, $\text{S}_2\text{O}_4^{2-}$, albeit with a rather long $\text{S}-\text{S}$ bond (p. 721). The trioxide ClO_3 is also predominantly dimeric in the condensed phase (see below) as probably is BrO_2 (p. 850).

The gaseous molecule of Cl_2O_7 has C_2 symmetry (Fig. 17.16) the ClO_3 groups being twisted 15° from the staggered (C_{2v}) configuration; the $\text{Cl}-\text{O}_\mu$ bonds are also inclined

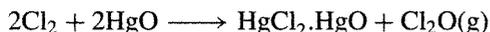
Table 17.19 Physical and molecular properties of the oxides of chlorine

Property	Cl_2O	ClO_2	ClOClO_3	$\text{Cl}_2\text{O}_6(\text{l})$ ($\rightleftharpoons 2\text{ClO}_3(\text{g})$)	Cl_2O_7
Colour and form at room temperature	Yellow-brown gas	Yellow-green gas	Pale yellow liquid	Dark red liquid	Colourless liquid
Oxidation states of Cl	+1	+4	+1, +7	+6	+7
MP/°C	-120.6	-59	-117	3.5	-91.5
BP/°C	2.0	11	44.5 (extrap)	203 (extrap)	81
$d(\text{liq}, 0^\circ\text{C})/\text{g cm}^{-3}$	—	1.64	1.806	—	2.02
$\Delta H_f^\circ(\text{gas}, 25^\circ\text{C})/\text{kJ mol}^{-1}$	80.3	102.6	~180	(155)	272
$\Delta G_f^\circ(\text{gas}, 25^\circ\text{C})/\text{kJ mol}^{-1}$	97.9	120.6	—	—	—
$S^\circ(\text{gas}, 25^\circ\text{C})/\text{J K}^{-1} \text{mol}^{-1}$	265.9	256.7	327.2	—	—
Dipole moment $\mu/\text{D}^{(a)}$	0.78 ± 0.08	1.78 ± 0.01	—	—	0.72 ± 0.02

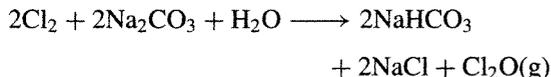
^(a) 1 D $\equiv 3.3356 \times 10^{-30}$ C m.

at an angle of 4.7° to the three-fold axis of the ClO_3 groups and there is a substantial decrease from the (single-bonded) $\text{Cl}-\text{O}_\mu$ to the (multiple-bonded) $\text{Cl}-\text{O}_t$ distance. A recent X-ray crystal structure analysis at -160° confirmed the C_2 symmetry of Cl_2O_7 and found $\text{Cl}-\text{O}_\mu$ 172.3 pm, $\text{Cl}-\text{O}_t$ (av.) 141.6 pm.⁽⁹⁹⁾ By contrast an X-ray examination of crystalline Cl_2O_6 at -70° revealed a mixed-valence ionic compound $[\text{Cl}^{\text{V}}\text{O}_2]^+[\text{Cl}^{\text{VII}}\text{O}_4]^-$ in which the angular ClO_2^+ and tetrahedral ClO_4^- ions were arranged in a distorted CsCl-type structure.⁽¹⁰⁰⁾ ClO_2^+ has $\text{Cl}-\text{O}$ 140.8 pm, angle OCIO 118.9° ; ClO_4^- has $\text{Cl}-\text{O}$ (av) 144.3 pm. The structures of the other oxides of chlorine have not been rigorously established.

We next consider the synthesis and chemical reactions of the oxides of chlorine. Because the compounds are strongly endothermic and have large positive free energies of formation it is not possible to prepare them by direct reaction of Cl_2 and O_2 . Dichlorine monoxide, Cl_2O , is best obtained by treating freshly prepared yellow HgO and Cl_2 gas (diluted with dry air or by dissolution in CCl_4):



The reaction is convenient for both laboratory scale and industrial preparations. Another large-scale process is the reaction of Cl_2 gas on moist Na_2CO_3 in a tower or rotary tube reactor:



Cl_2O is very soluble in water, a saturated solution at -9.4°C containing 143.6 g Cl_2O per 100 g H_2O ; in fact the gas is the anhydride of hypochlorous acid, with which it is in equilibrium in aqueous solutions:

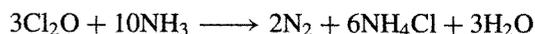


⁹⁹ A. SIMON and H. BORRMANN, *Angew. Chem. Int. Edn. Engl.* **27**, 1339–41 (1988).

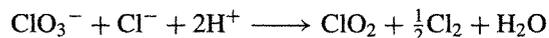
¹⁰⁰ K. M. TOBIAS and M. JANSEN, *Z. anorg. allg. Chem.* **550**, 16–26 (1987).

Much of the Cl_2O manufactured industrially is used to make hypochlorites, particularly $\text{Ca}(\text{OCl})_2$, and it is an effective bleach for wood-pulp and textiles. Cl_2O is also used to prepare chloroisocyanurates (p. 324) and chlorinated solvents (via mixed chain reactions in which Cl and OCl are the chain-propagating species).⁽¹⁰¹⁾ Its reactions with inorganic reagents are summarized in the scheme opposite.

Gaseous mixtures of Cl_2O and NH_3 explode violently: the overall stoichiometry of the reaction can be represented as

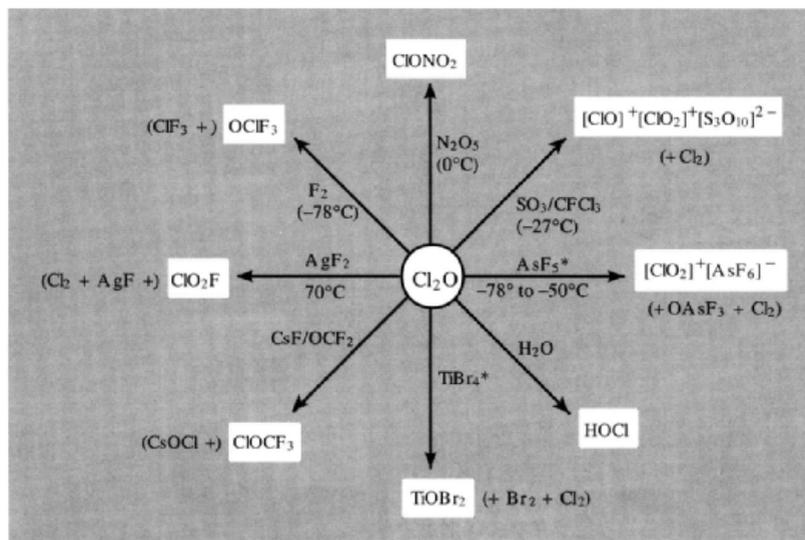


Chlorine dioxide, ClO_2 , was the first oxide of chlorine to be discovered and is now manufactured on a massive scale for the bleaching of wood-pulp and for water treatment;^(98,102) however, because of its explosive character as a liquid or concentrated gas, it must be made at low concentrations where it is to be used. For this reason, production statistics can only be estimated, but it is known that its use in the US wood-pulp and paper industry increased tenfold from 7800 tonnes in 1955 to 78 800 tonnes in 1970; thereafter captive production for this purpose increased less rapidly but the total US production of this gas for all purposes reached 361 000 tonnes in 1990. Production in Canada paralleled this growth and was 200 000 tonnes in 1990. Prices in 1992 were in the range \$1100–1800/tonne. Usually ClO_2 is prepared by reducing NaClO_3 with NaCl , HCl , SO_2 or MeOH in strongly acid solution; other reducing agents that have been used on a laboratory scale include oxalic acid, N_2O , EtOH and sugar. With Cl^- as reducing agent the formal reaction can be written:



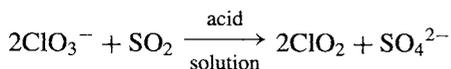
¹⁰¹ J. J. RENARD and H. I. BOLKER, *Chem. Revs.* **76**, 487–505 (1976).

¹⁰² W. J. MASSCHELEIN, *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds*, Ann Arbor Science Publishers, Ann Arbor, 1979, 190 pp. J. KATZ (ed.), *Ozone and Chlorine Dioxide Technology for Disinfection of Drinking Water*, Noyes Data Corp., Park Ridge, New Jersey, 1980, 659 pp.

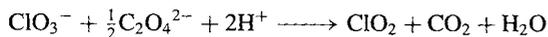


Scheme Some reactions of dichlorine monoxide. *[In addition $\text{AsCl}_3 \rightarrow \text{AsO}_2\text{Cl}$; $\text{SbCl}_5 \rightarrow \text{SbO}_2\text{Cl}$; $\text{VOCl}_3 \rightarrow \text{VO}_2\text{Cl}$; $\text{TiCl}_4 \rightarrow \text{TiOCl}_2$.]⁽¹⁰¹⁾

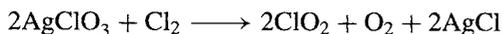
Contamination of the product with Cl_2 gas is not always undesirable but can be avoided by using SO_2 :



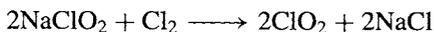
On a laboratory scale reduction of KClO_3 with moist oxalic acid generates the gas suitably diluted with oxides of carbon:



Samples of pure ClO_2 for measurement of physical properties can be obtained by chlorine reduction of silver chlorate at 90°C :



Chlorine oxidation of sodium chlorite has also been used on both an industrial scale (by mixing concentrated aqueous solutions) or on a laboratory scale (by passing Cl_2 /air through a column packed with the solid chlorite):



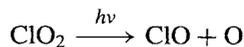
The production of ClO_2 obviously hinges on the redox properties of oxochlorine species (p. 853)

and, indeed, the gas was originally obtained simply by the (extremely hazardous) disproportionation of chloric acid liberated by the action of concentrated sulfuric acid on a solid chlorate:

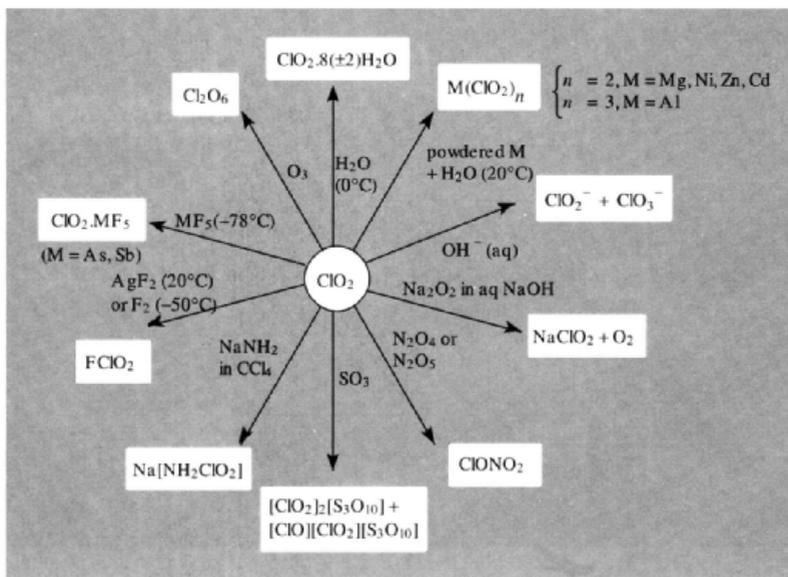


ClO_2 is a strong oxidizing agent towards both organic and inorganic materials and it reacts readily with S, P, PX_3 and KBH_4 . Some further reactions are in the scheme overleaf:⁽⁹⁷⁾

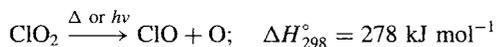
ClO_2 dissolves exothermically in water and the dark-green solutions, containing up to 8 g/l, decompose only very slowly in the dark. At low temperatures crystalline clathrate hydrates, $\text{ClO}_2 \cdot n\text{H}_2\text{O}$, separate ($n \approx 6-10$). Illumination of neutral aqueous solutions initiates rapid photodecomposition to a mixture of chloric and hydrochloric acids:



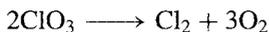
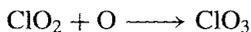
By contrast, alkaline solutions hydrolyse vigorously to a mixture of chlorite and chlorate (see scheme overleaf).



The photochemical and thermal decomposition of ClO_2 both begin by homolytic scission of a Cl–O bond:



Subsequent reactions depend on conditions. Ultraviolet photolysis of isolated molecules in an inert matrix yields the radicals ClO and ClOO . At room temperature, photolysis of dry gaseous ClO_2 yields Cl_2 , O_2 , and some ClO_3 which either dimerizes or is further photolysed to Cl_2 and O_2 :



By contrast, photolysis of solid ClO_2 at -78°C produces some Cl_2O_3 as well as Cl_2O_6 :



The ClO radical in particular is implicated in environmentally sensitive reactions which lead to depletion of ozone and oxygen atoms in the

stratosphere.⁽¹⁰³⁾ Thus (as was first pointed out by M. J. Molina and F. S. Rowland in 1974⁽¹⁰⁴⁾) chlorofluorocarbons such as CFCl_3 and CF_2Cl_2 , which have been increasingly used as aerosol spray propellants, refrigerants, solvents and plastic foaming agents (p. 304), have penetrated the stratosphere (10–50 km above the earth's surface) where they are photolysed or react with electronically excited $\text{O}(^1D)$ atoms to yield Cl atoms and chlorine oxides; this leads to the continuous removal of O_3 and O atoms via such reactions as:



i.e. $\text{O} + \text{O}_3 \longrightarrow 2\text{O}_2$ plus regeneration of Cl

Depletion of O_3 results in an increased penetration of ultraviolet light with wavelengths in the range 290–320 nm which may in time effect changes in climate and perhaps lead also to an increased incidence of skin cancer in

¹⁰³ R. J. DONOVAN, *Educ. in Chem.* **15**, 110–13 (1978).
B. A. THRUSH, *Endeavour (New Series)* **1**, 3–6 (1977), and references therein.

¹⁰⁴ M. J. MOLINA and F. S. ROWLAND, *Nature* **249**, 810–12 (1974).

humans. Because of these concerns, the alarming increase in global sales of chlorofluorocarbons, which grew 15-fold between 1948 and 1973, has since been drastically reduced as shown by the following illustrative figures for CFC-11 and CFC-12 (tonnes):

	1948	1973	1983
CFCl ₃ (CFC-11)	2 270	302 000	93 000
CF ₂ Cl ₂ (CFC-12)	2 220	383 000	120 000

The decrease is continuing due to global adherence to the provisions of the Montreal (1989) and London (1990) Protocols, and it is hoped that the most deleterious CFCs will eventually be phased out completely. As a result of their work, Rowland and Molina were awarded the Nobel Prize for Chemistry for 1995 (together with P. Crutzen, who showed how NO and NO₂ could similarly act as catalysts for the depletion of stratospheric ozone). Several excellent accounts giving more details of the chemistry and meteorology involved are available.^(105–108)

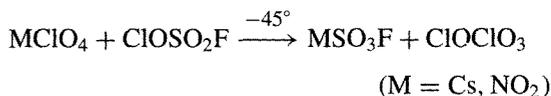
The great importance of the short-lived ClO radical has stimulated numerous investigations of its synthesis and molecular properties. Several routes are now available to this species (some of which have already been indicated above):

- thermal decomposition of ClO₂ or ClO₃;
- decomposition of FClO₃ in an electric discharge;
- passage of a microwave or radio-frequency discharge through mixtures of Cl₂ and O₂;
- reactions of Cl atoms with ClO or O₃ at 300 K;

- gas-phase photolysis of Cl₂O, ClO₂ or mixtures of Cl₂ and O₂.

It is an endothermic species with $\Delta H_f^\circ(298\text{ K})$ 101.8 kJ mol⁻¹, $\Delta G_f^\circ(298\text{ K})$ 98.1 kJ mol⁻¹, $S^\circ(298\text{ K})$ 226.5 J K⁻¹ mol⁻¹. The interatomic distance Cl–O is 156.9 pm, its dipole moment is 1.24 D, and the bond dissociation energy D_0 is 264.9 kJ mol⁻¹ (cf. BrO p. 851, IO p. 853).

Chlorine perchlorate ClOClO₃ is made by the following low-temperature reaction:



Little is known of its structure and properties; it is even less stable than ClO₂ and decomposes at room temperature to Cl₂, O₂ and Cl₂O₆.

Dichlorine hexoxide, Cl₂O₆, is best made by ozonolysis of ClO₂:



The dark-red liquid freezes to a solid which is yellow at –180°C. The structure in the liquid phase is not known but two possibilities have been considered. The Cl–Cl linked structure is superficially attractive as the product of dimerization of the paramagnetic gaseous species ClO₃, but magnetic susceptibility studies of the equilibrium Cl₂O₆ ⇌ 2ClO₃ in the liquid phase were flawed by the subsequent finding that there was no esr signal from ClO₃ and that ClO₂ (as an impurity) was the sole paramagnetic species present. Accordingly, the much-quoted value of 7.24 kJ mol⁻¹ for the derived heat of dimerization is without foundation. The alternative oxygen-bridged dimer, though requiring more electronic and geometric rearrangement of the presumed pyramidal *ClO₃ monomers, is rather closer to the ionic structure [ClO₂]⁺[ClO₄]⁻ which has been established by X-ray analysis (p. 846) of the solid. Cl₂O₆ does, in fact, frequently behave as chloryl perchlorate in its reactions though experience with N₂O₄ as “nitrosyl nitrate” (p. 455) engenders caution in attempting to deduce a geometrical structure from chemical reactions (cf. however, diborane, p. 165).

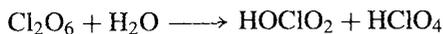
¹⁰⁵ F. S. ROWLAND and M. J. MOLINA, *Chem. & Eng. News*, August 15, 8–13 (1994).

¹⁰⁶ M. J. MOLINA and L. T. MOLINA, Chap. 2 in D. A. DUNNETTE and R. J. O'BRIEN (eds.), *The Science of Global Change: The Impact of Human Activities on the Environment*, ACS Symposium Series 483, 24–35 (1992).

¹⁰⁷ R. P. WAYNE, *Chemistry of Atmospheres*, (2nd. edn.), Oxford University Press, Oxford, 1991, 456 pp.

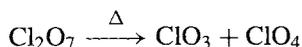
¹⁰⁸ P. S. ZURER, *Chem. & Eng. News*, May 24, 8–18 (1993). See also P. S. ZURER, *Chem. & Eng. News*, Jan. 2, 30–2 (1989) and Mar. 6, 29–31 (1989).

Hydrolysis of Cl_2O_6 gives a mixture of chloric and perchloric acids, whereas anhydrous HF sets up an equilibrium:



Nitrogen oxides and their derivatives displace ClO_2 to form nitrosyl and nityl perchlorates. These and other reactions are summarized in the scheme below.

Dichlorine heptoxide, Cl_2O_7 , is the anhydride of perchloric acid (p. 865) and is conveniently obtained by careful dehydration of HClO_4 with H_3PO_4 at -10°C followed by cautious low-pressure distillation at -35°C and 1 mmHg. The compound is a shock-sensitive oily liquid with physical properties and structure as already described (p. 845). Cl_2O_7 is less reactive than the lower oxides of chlorine and does not ignite organic materials at room temperature. Dissolution in water or aqueous alkalis regenerates perchloric acid and perchlorates respectively. Thermal decomposition (which can be explosive) is initiated by rupture of a $\text{Cl}-\text{O}_\mu$ bond, the activation energy being $\sim 135 \text{ kJ mol}^{-1}$:



Oxides of bromine

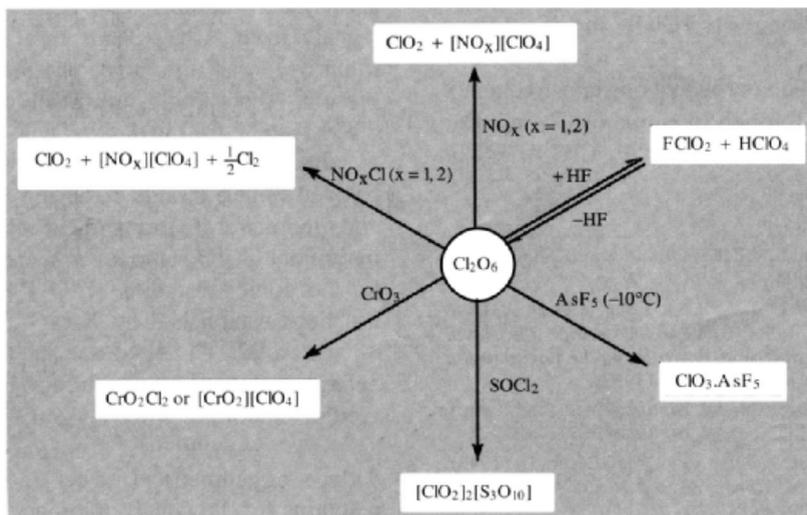
The oxides of Br are less numerous, far less studied, and much less well characterized than the ten oxide species of chlorine discussed in the preceding section. The reasonably well established compounds are listed below.

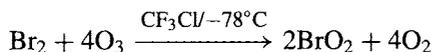
Br_2O : a dark-brown solid moderately stable at -60° (mp -17.5° with decomposition), prepared by reaction of Br_2 vapour on HgO (cf. Cl_2O p. 846) or better, by low-temperature vacuum decomposition of BrO_2 . The molecule has C_{2v} symmetry in both the solid and vapour phase with $\text{Br}-\text{O}$ $185 \pm 1 \text{ pm}$ and angle BrOBr $112 \pm 2^\circ$ as determined by EXAFS (extended X-ray absorption fine structure).⁽¹⁰⁹⁾ It oxidizes I_2 to I_2O_5 , benzene to 1,4-quinone, and yields OBr^- in alkaline solution.

“ BrO_2 ”: a pale yellow crystalline solid formed quantitatively by low-temperature ozonolysis of Br_2 :[†]

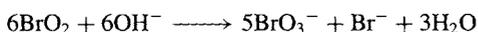
¹⁰⁹ W. LEVASON, J. S. OGDEN, M. D. SPICER and N. A. YOUNG, *J. Am. Chem. Soc.* **112**, 1019–22 (1990).

[†] Ozonolysis of Br_2 at 0°C yields white, poorly characterized solids which, depending on the conditions used, have compositions close to Br_2O_5 , Br_3O_8 , and BrO_3 ; no structural data are available.





The structure has recently been shown by EXAFS to be bromine perbromate BrOBrO_3 with $\text{Br}^{\text{I}}-\text{O}$ 186.2 pm, $\text{Br}^{\text{VII}}-\text{O}$ 160.5 pm and angle BrOBr $110 \pm 3^\circ$;⁽¹¹⁰⁾ (cf. ClOClO_3 and BrOClO_3). BrOBrO_3 is thermally unstable above -40°C and decomposes violently to the elements at 0°C ; slower warming yields BrO_2 (see above). Alkaline hydrolysis leads to disproportionation:



Reaction with F_2 yields FBrO_2 and with N_2O_4 yields $[\text{NO}_2]^+[\text{Br}(\text{NO}_3)_2]^-$.

Br_2O_3 : an orange crystalline solid very recently isolated at -90° from CH_2Cl_2 solution after ozonization of Br_2 in CFCl_3 . It decomposes above -40° , detonates if warmed rapidly to 0° , and was shown by X-ray analysis to be *syn*- BrOBrO_2 with $\text{Br}^{\text{I}}-\text{O}$ 184.5 pm, $\text{Br}^{\text{V}}-\text{O}$ 161.3 pm and angle BrOBr 111.6° .⁽¹¹¹⁾ It is thus, formally, the anhydride of hypobromous and bromic acids.

In addition to these compounds the unstable monomeric radicals BrO , BrO_2 and BrO_3 have been made by γ -radiolysis or flash photolysis of the anions OBr^- , BrO_2^- and BrO_3^- . For BrO the interatomic distance is 172.1 pm, the dipole moment 1.55 D, and the thermodynamic properties $\Delta H_f^\circ(298\text{ K})$ 125.8 kJ mol^{-1} , $\Delta G_f^\circ(298\text{ K})$ 108.2 kJ mol^{-1} and $S^\circ(298\text{ K})$ 237.4 $\text{J K}^{-1} \text{mol}^{-1}$. Most recently⁽¹¹²⁾ it has been shown that flash pyrolysis at $800\text{--}1000^\circ\text{C}$ of a mixture containing $\text{Br}_2/\text{O}_2/\text{Ar}$ yields bromine superoxide, $[\text{BrOO}]^*$, which can be trapped at 12 K and shown by ir- and uv-spectroscopy to be non-linear. Irradiation of

this species at 254 nm results in isomerization to bromine dioxide, $[\text{OBrO}]^*$, which is also non-linear (angle $\sim 110^\circ$) and which can be reconverted to the superoxide by irradiating the matrix at wavelengths greater than 360 nm.

Oxides of iodine

Iodine forms the most stable oxides of the halogens and I_2O_5 was made (independently) by J. L. Gay Lussac and H. Davy in 1813. However, despite this venerable history the structure of the compound was not determined unambiguously until 1970. It is most conveniently prepared by dehydrating iodic acid (p. 863) at 200°C in a stream of dry air but it also results from the direct oxidation of I_2 with oxygen in a glow discharge. The structure (Fig. 17.17) features molecular units of O_2IOIO_2 formed by joining two pyramidal IO_3 groups at a common oxygen. The bridging I–O distances correspond to single bonds, whereas the terminal I–O distances are substantially shorter.⁽¹¹³⁾ There are also appreciable intermolecular interactions which join the molecular units into cross-linked chains; this gives each iodine pseudo-fivefold coordination, the sixth position of the distorted

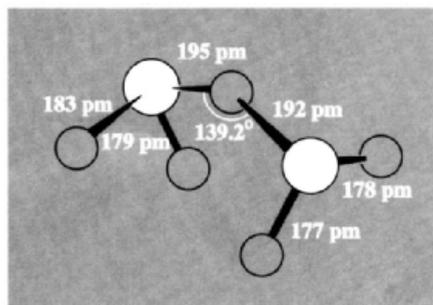


Figure 17.17 The structure of I_2O_5 showing the dimensions and conformation of a single molecular unit. Note that the molecule has no mirror plane of symmetry so is not C_{2v} .

¹¹⁰ T. R. GILSON, W. LEVASON, J. S. OGDEN, M. D. SPICER and N. A. YOUNG, *J. Am. Chem. Soc.* **114**, 5469–70 (1992).

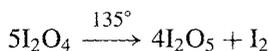
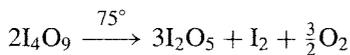
¹¹¹ R. KUSCHEL and K. SEPPALT, *Angew. Chem. Int. Edn. Engl.* **32**, 1632–3 (1993).

¹¹² G. MAIER and A. BOTHUR, *Z. anorg. allg. Chem.* **621**, 743–6 (1995).

¹¹³ K. SELTE and A. KJEKSHUS, *Acta Chem. Scand.* **24**, 1912–24 (1970).

octahedron presumably being occupied by the lone-pair of electrons on the iodine atom.

I_2O_5 forms white, hygroscopic, thermodynamically stable crystals: $\Delta H_f^\circ -158.1 \text{ kJ mol}^{-1}$, d 4.980 g cm^{-3} . The compound is very soluble in water, reforming the parent acid HIO_3 . So great is the affinity for water that commercial " I_2O_5 " consists almost entirely of HI_3O_8 , i.e. $I_2O_5 \cdot HIO_3$. The interrelations between these compounds and the rather less stable oxides I_4O_9 and I_2O_4 are shown in the scheme below. I_4O_9 is a hygroscopic yellow powder which decomposes to I_2O_5 when heated above 75° ; I_2O_4 forms diamagnetic lemon-yellow crystals (d 4.2 g cm^{-3}) which start to decompose above 85° and which rapidly yield I_2O_5 at 135° :



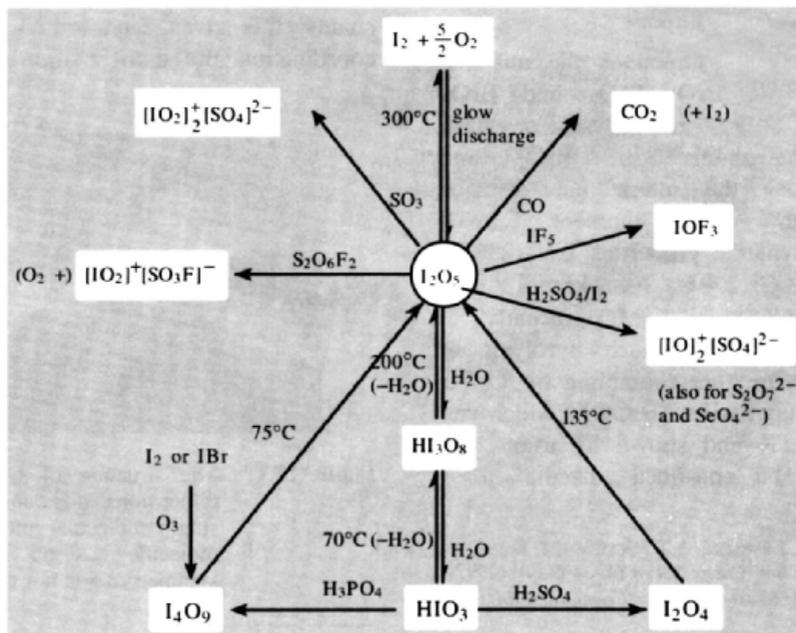
The structure of these oxides are unknown but I_4O_9 has been formulated as $I^{III}(I^V O_3)_3$ and I_2O_4 as $[IO]^{+}[IO_3]^{-}$.

I_2O_5 is notable in being one of the few chemicals that will oxidize CO rapidly and completely at room temperature:



The reaction forms the basis of a useful analytical method for determining the concentration of CO in the atmosphere or in other gaseous mixtures. I_2O_5 also oxidizes NO, C_2H_4 and H_2S . SO_3 and $S_2O_6F_2$ yield iodyl salts, $[IO_2]^{+}$, whereas concentrated H_2SO_4 and related acids reduce I_2O_5 to iodosyl derivatives, $[IO]^{+}$. Fluorination of I_2O_5 with F_2 , BrF_3 , SF_4 or $FCIO_2$ yields IF_5 which itself reacts with the oxide to give OIF_3 . It is also convenient to note here other related compounds which have recently been characterized: $I(OTeF_5)_3$, $O=I(OTeF_5)_3$, $I(OTeF_5)_5$, $[I(OTeF_5)_4]^{-}$ and $[O=I(OTeF_5)_4]^{-}$; ⁽¹¹⁴⁾ all have the expected structures (cf. pp. 688, 777, 899, 904).

¹¹⁴ L. TUROWSKY and K. SEPELT, *Z. anorg. allg. Chem.* **602**, 79–87 (1991), and references cited therein.



SCHEME: Preparation of reactions of iodine oxides.