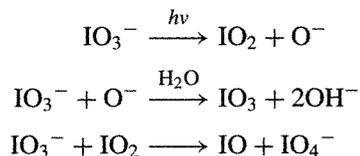


In addition to the stable  $I_2O_5$  and moderately stable  $I_4O_9$  and  $I_2O_4$ , several short-lived radicals have been detected and characterized during  $\gamma$ -radiolysis and flash photolysis of iodates in aqueous alkali:



The endothermic radical IO has also been studied in the gas phase: the interatomic distance is 186.7 pm and the bond dissociation energy  $\sim 175 \pm 20 \text{ kJ mol}^{-1}$ . It thus appears that, although the higher oxides of iodine are much more stable than any oxide of Cl or Br, nevertheless, IO is much less stable than ClO (p. 849) or BrO (p. 851). Its enthalpy of formation and other thermodynamic properties are:  $\Delta H_f^\circ(298 \text{ K}) 175.1 \text{ kJ mol}^{-1}$ ,  $\Delta G_f^\circ(298 \text{ K}) 149.8 \text{ kJ mol}^{-1}$ ,  $S^\circ(298 \text{ K}) 245.5 \text{ J K}^{-1} \text{ mol}^{-1}$ .

### 17.2.8 Oxoacids and oxoacid salts

#### General considerations<sup>(115)</sup>

The preparative chemistry and technical applications of the halogen oxoacids and their salts have been actively pursued and developed for over two centuries (p. 790) and can now be very satisfactorily systematized in terms of general

thermodynamic principles. The thermodynamic data are codified in the form of reduction potentials and equilibrium constants and these, coupled with the relative rates of competing reactions, allow a vast range of aqueous solution chemistry of the halogens to be interrelated. Thus, although all the halogens are to some extent soluble in water, extensive disproportionation reactions and/or mutual redox reactions with the solvent can occur to an extent that depends crucially on conditions such as pH and concentration (which influence the thermodynamic variables) and the presence of catalysts or light quanta (which can overcome kinetic activation barriers). Fluorine is again exceptional and, because of its very high standard reduction potential,  $E^\circ(\frac{1}{2}F_2/F^-) + 2.866 \text{ V}$ , reacts very strongly with water at all values of pH (p. 629). Its inability to achieve formal oxidation states higher than +1 also limits the available oxoacids to hypofluorous acid HOF (p. 856). Numerous other oxoacids are known for the heavier halogens (Table 17.20) though most cannot be isolated pure and are stable only in aqueous solution or in the form of their salts. Anhydrous perchloric acid ( $HClO_4$ ), iodic acid ( $HIO_3$ ), paraperiodic acid ( $H_5IO_6$ ) and metaperiodic acid ( $HIO_4$ ) have been isolated as pure compounds.

The standard reduction potentials for Cl, Br and I species in acid and in alkaline aqueous solutions are summarized in Fig. 17.18. The couples  $\frac{1}{2}X_2/X^-$  are independent of pH and, together with the value for  $F_2$ , indicate a steadily decreasing oxidizing power of the halogens in the sequence  $F_2(+2.866 \text{ V}) > Cl_2(+1.358 \text{ V}) > Br_2(+1.066 \text{ V}) > I_2(+0.536 \text{ V})$ . Remembering

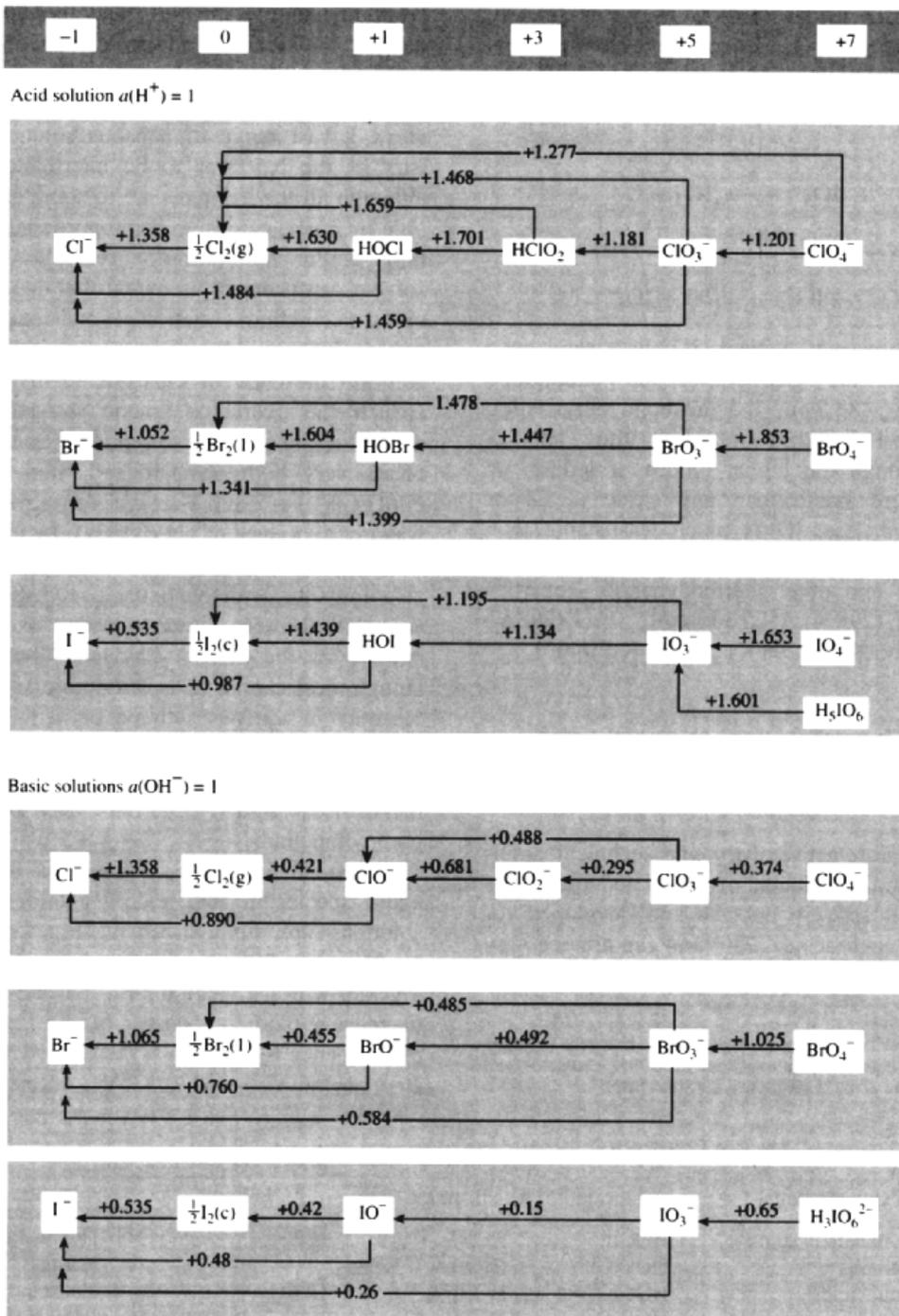
<sup>115</sup> Ref. 23, Chemical properties of the halogens — redox properties: aqueous solutions, pp. 1188–95; Oxoacids and oxoacid salts of the halogens, pp. 1396–1465.

**Table 17.20** Oxoacids of the halogens

Generic name	Chlorine	Bromine	Iodine	Salts
Hypohalous acids <sup>(b)</sup>	HOCl <sup>(a)</sup>	HOBr <sup>(a)</sup>	HOI <sup>(a)</sup>	Hypohalites
Halous acids	HOClO <sup>(a)</sup>	(HOBrO?) <sup>(a)</sup>	—	Halites
Halic acids	HOClO <sub>2</sub> <sup>(a)</sup>	HOBrO <sub>2</sub> <sup>(a)</sup>	HOIO <sub>2</sub>	Halates
Perhalic acids	HOClO <sub>3</sub>	HOBrO <sub>3</sub> <sup>(a)</sup>	HOIO <sub>3</sub> , (HO) <sub>5</sub> IO, H <sub>4</sub> I <sub>2</sub> O <sub>7</sub>	Perhalates

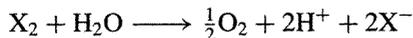
<sup>(a)</sup>Stable only in aqueous solution.

<sup>(b)</sup>HOF also known (p. 856).



**Figure 17.18** Standard reduction potentials for Cl, Br and I species in acid and alkaline solutions. For At see p. 886.

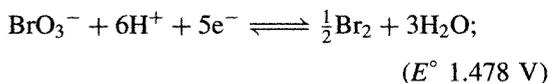
that  $E^\circ(\frac{1}{2}\text{O}_2/\text{H}_2\text{O}) = 1.229\text{ V}$  these values indicate that the potentials for the reaction.



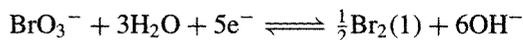
decrease in the sequence  $\text{F}_2(+1.637\text{ V}) > \text{Cl}_2(+0.129\text{ V}) > \text{Br}_2(-0.163\text{ V}) > \text{I}_2(-0.693\text{ V})$ . As already mentioned, this implies that  $\text{F}_2$  will oxidize water to  $\text{O}_2$  and the same should happen with chlorine in the absence of sluggish kinetic factors. In fact, were it not for the further fortunate circumstance of an appreciably higher overvoltage for oxygen, chlorine would not be evolved during the electrolysis of aqueous chloride solutions at low current densities: the phenomenon is clearly of great technical importance for the industrial preparation of chlorine by electrolysis of brines (p. 798).

For all other couples in Fig. 17.18 (i.e. for all couples involving oxygenated species) an increase in pH causes a dramatic reduction in  $E^\circ$  as expected (p. 435). For example, in acid solution the couple  $\text{BrO}_3^-/\frac{1}{2}\text{Br}_2(\text{l})$  refers to the

equilibrium reaction



The equilibrium constant clearly depends on the sixth power of the hydrogen-ion concentration and, when this is reduced (say to  $10^{-14}$  in 1 M alkali), the potential is likewise diminished by an amount  $\sim(RT/nF)\log_{10}[\text{H}^+]^6$ , i.e. by *ca.*  $(0.0592/5) \times 14 \times 6 \simeq 0.99\text{ V}$ . In agreement with this (Fig. 17.18) the potential at pH 14 is 0.485 V (calc  $\sim 0.49\text{ V}$ ) for the reaction



The data in Fig. 17.18 are presented in graphical form in Fig. 17.19 which shows the volt-equivalent diagrams (p. 436) for acid and alkaline solutions. It is clear from these that  $\text{Cl}_2$  and  $\text{Br}_2$  are much more stable towards disproportionation in acid solution (concave angle at  $\text{X}_2$ ) than in alkaline solutions (convex angle of

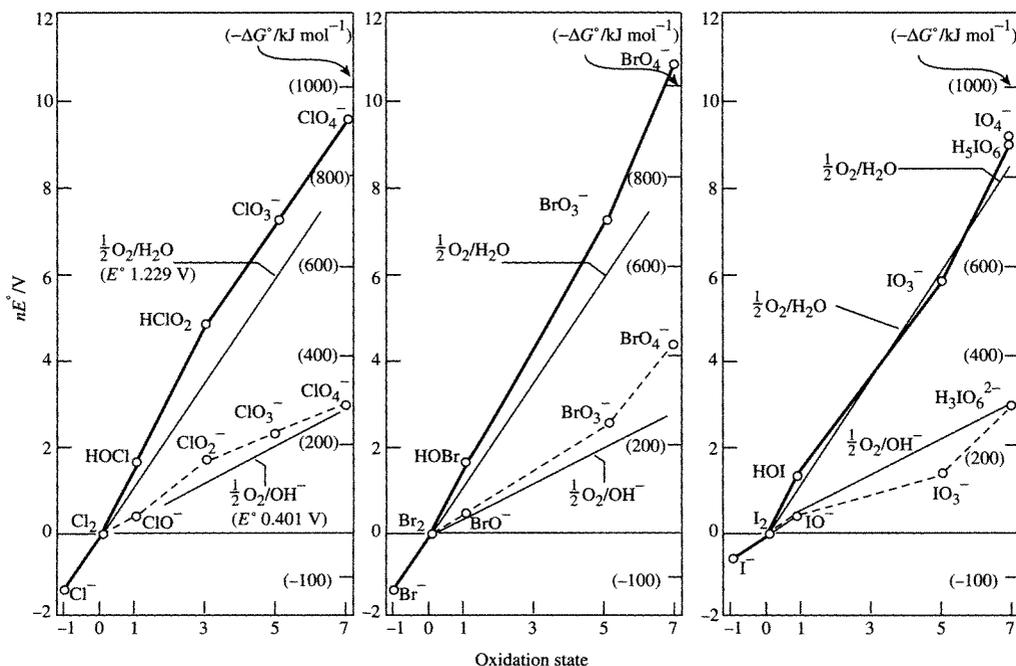
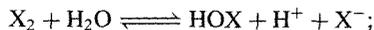


Figure 17.19 Volt-equivalent diagrams for Cl, Br and I.

equilibrium constants:

acid solution :



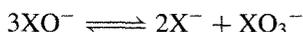
$$K_{ac} = \frac{[HOX][H^+][X^-]}{[X_2]}$$

alkaline solution :

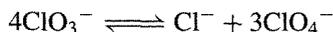


$$K_{alk} = \frac{[OX^-][X^-]}{[X_2][OH^-]^2}$$

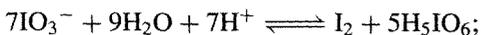
For  $Cl_2$ ,  $Br_2$  and  $I_2$ ,  $K_{ac}$  is  $4.2 \times 10^{-4}$ ,  $7.2 \times 10^{-9}$  and  $2.0 \times 10^{-13} \text{ mol}^2 \text{ l}^{-2}$  respectively, thereby favouring the free halogens, whereas  $K_{alk}$  is  $7.5 \times 10^{15}$ ,  $2 \times 10^8$  and  $30 \text{ mol}^{-1} \text{ l}$  respectively, indicating a tendency to disproportionation which is overwhelming for  $Cl_2$  but progressively less pronounced for  $Br_2$  and  $I_2$ . In actuality the situation is somewhat more complicated because of the tendency of the hypohalite ions themselves to disproportionate further to produce the corresponding halite ions:



The equilibrium constant for this reaction is very favourable in each case:  $10^{27}$  for  $ClO^-$ ,  $10^{15}$  for  $BrO^-$ , and  $10^{20}$  for  $IO^-$ . However, particularly in the case of  $ClO^-$ , the rate of disproportionation is slow at room temperature and only becomes appreciable above  $70^\circ$ . Similarly, the disproportionation



has an equilibrium constant of  $10^{20}$  but the reaction is very slow even at  $100^\circ$ . By contrast, as indicated by the concavity of the volt-equivalent curve at  $BrO_3^-$  and  $IO_3^-$  (Fig. 17.19), the bromate and iodate ions are stable with respect to disproportionation (in both acid and alkaline solutions), e.g.:

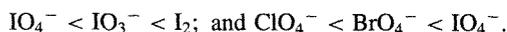
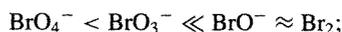
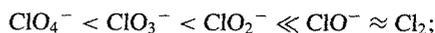


$$K = 10^{-85} \text{ mol}^{-8} \text{ l}^8$$



$$K = 10^{-44} \text{ mol}^{-3} \text{ l}^3$$

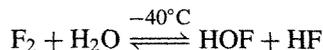
More detailed consideration of these various equilibria and other redox reactions of the halogen oxoacids will be found under the separate headings below. As expected, the rates of redox reactions of the halogen oxyanions will depend, sometimes crucially, on the precise conditions used. However, as a very broad generalization, they tend to become progressively faster as the oxidation state of the halogen decreases, i.e.:



The strengths of the monobasic acids increase rapidly with increase in oxidation state of the halogen in accordance with Pauling's rules (p. 50). For example, approximate values of  $pK_a$  are:  $HOCl$  7.52,  $HOClO$  1.94,  $HOClO_2$  - 3,  $HOClO_3$  - 10. The  $pK_a$  values of related acids increase in the sequence  $Cl < Br < I$ .

#### Hypohalous acids, HOX, and hypohalites, $XO^-$ (98,115)

Hypofluorous acid is the most recent of the halogen oxoacids to be prepared.<sup>(116)</sup> Traces were obtained in 1968 by photolysis of a mixture of  $F_2$  and  $H_2O$  in a matrix of solid  $N_2$  at 14–20 K but weighable amounts of the compound were first obtained by M. H. Studier and E. H. Appelman in 1971 by the fluorination of ice:



The isolation of HOF depends on removing it rapidly from the reaction zone so that it is prevented from reacting further with HF,  $F_2$  or  $H_2O$  (see below). The method used was to recirculate  $F_2$  at  $\sim 100 \text{ mmHg}$  through a Kel-F U-tube filled with moistened Räschi rings cut from Teflon "spaghetti" tubing (Kel-F is polymerized chlorotrifluoroethene; Teflon is polymerized tetrafluoroethene). The U-tube was held at about  $-40^\circ C$  and the effluent was passed through U-tubes cooled to  $-50^\circ$  and  $-79^\circ$  to

<sup>116</sup> E. H. APPELMAN, *Acc. Chem. Res.* 6, 113–7 (1973).

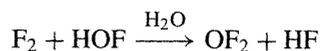
remove water and HF, and, finally, through a U-tube at  $-183^\circ$  to trap the HOF. The use of the  $-50^\circ$  trap was found to be critical because without it all of the HOF was caught in the  $-79^\circ$  with the  $\text{H}_2\text{O}$ , from which it could not be isolated because of subsequent reaction.

HOF is a white solid which melts at  $-117^\circ$  to a pale-yellow liquid. Its bp (extrap) is somewhat below room temperature and its volatility is thus comparable to that of HF with which it is always slightly contaminated. Spectroscopic data establish a nonlinear structure with H–O 96.4 pm, O–F 144.2 pm, and bond angle H–O–F  $97.2^\circ$ : this is the smallest known bond angle at an unrestricted O atom (cf. H–O–H  $104.7^\circ$ , F–O–F  $103.2^\circ$ ). It has been suggested that this arises in part from electrostatic attraction of the 2 terminal atoms, since nmr data lead to a charge of  $\sim +0.5e$  on H and  $\sim -0.5e$  on F. The negative charge on F is intermediate between those estimated for F in HF and  $\text{OF}_2$  and this emphasizes the strictly formal nature of the +1 oxidation state for F in HOF. Subsequently, the crystal structure of HOF was determined at  $-160^\circ$  in an experimental *tour de force*.<sup>(117)</sup> The dimensions were similar to those found for the gaseous molecule except for the expected artefact of a slightly shorter H–O distance due to the X-ray method (H–O 0.78 pm, O–F 144.2 pm, angle HOF  $101^\circ$ ). The molecules are arranged in chains along a screw axis parallel to the *b* axis of the crystal as a result of almost linear O–H $\cdots$ O bonds (angle  $163^\circ$ , O $\cdots$ O 289.5 pm).

The most prominent chemical property of HOF is its instability. It decomposes spontaneously (sometimes explosively) to HF and  $\text{O}_2$  with a half-life of *ca.* 30 min in a Teflon apparatus at room temperature and 100 mmHg. It reacts rapidly with water to produce HF,  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ ; in dilute aqueous acid  $\text{H}_2\text{O}_2$  is the predominant product whereas in alkaline solution  $\text{O}_2$  is the principal O-containing product. The kinetics of these processes have been studied and, by use of  $^{18}\text{O}$ -enriched  $\text{H}_2\text{O}_2$ , it has

been shown, uniquely, that the  $\text{O}_2$  formed in the reaction,  $[\text{HOF} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{HF} + \text{H}_2\text{O}]$ , contains a substantial amount of oxygen from the HOF.<sup>(118)</sup>

HOF reacts with HF to reverse the equilibrium used in its preparation. It does not dehydrate to its formal anhydride  $\text{OF}_2$  but in the presence of  $\text{H}_2\text{O}$  it reacts with  $\text{F}_2$  to form this species.

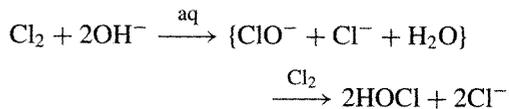


This reaction does not occur in the gas phase, however, in the absence of  $\text{H}_2\text{O}$ .

By contrast with the elusive though isolable HOF, the history of HOCl goes back over two centuries to the earliest experiments of C. W. Scheele with  $\text{Cl}_2$  in 1774 (p. 792), and the bleaching and sterilizing action of hypochlorites have long been used both industrially and domestically. HOCl, HOBr and HOI are all highly reactive, relatively unstable compounds that are known primarily in aqueous solutions. The most convenient preparation of such solutions is by perturbing the hydrolytic disproportionation equilibrium (p. 856):



by addition of  $\text{HgO}$  or  $\text{Ag}_2\text{O}$  so as to remove the halide ions. On an industrial scale, aqueous solutions of HOCl (containing  $\text{Cl}^-$ ) are readily prepared by reacting  $\text{Cl}_2$  with aqueous alkali. With strong bases  $\{\text{NaOH}, \text{Ca}(\text{OH})_2\}$  the reaction proceeds via the intermediate formation of hypochlorite, but this intermediate product is not formed with weaker bases such as  $\text{NaHCO}_3$  or  $\text{CaCO}_3$ :

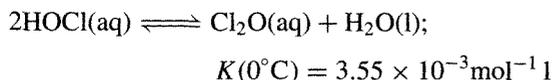


Chloride-free solutions (up to 5 M concentration) can be made by treating  $\text{Cl}_2\text{O}$  with water at  $0^\circ$  or industrially by passing  $\text{Cl}_2\text{O}$  gas into water. In fact, concentrated solutions of HOCl also contain appreciable amounts of  $\text{Cl}_2\text{O}$  which can form a

<sup>117</sup> W. POLL, G. PAWELKE, D. MOOTZ and E. H. APPELMAN, *Angew. Chem. Int. Edn. Engl.* **27**, 392–3 (1988).

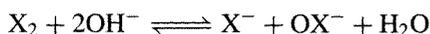
<sup>118</sup> E. H. APPELMAN and R. C. THOMPSON, *J. Am. Chem. Soc.*, **106**, 4167–72 (1984).

separate layer and which is probably the source of the yellow colour of such solutions:



Organic solutions can be obtained in high yield by extracting HOCl from  $\text{Cl}^-$ -containing aqueous solutions into polar solvents such as ketones, nitriles or esters. Electrodialysis using semipermeable membranes affords an alternative route.

Solutions of the corresponding hypohalites can be made by the rapid disproportionation of the individual halogens in cold alkaline solutions (p. 856):



Such solutions are necessarily contaminated with halide ions and with the products of any subsequent decomposition of the hypohalite anions themselves. Alternative routes are the electrochemical oxidation of halides in cold dilute solutions or the chemical oxidation of bromides and iodides:

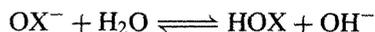


Hypochlorites can also be made by careful neutralization of aqueous solutions of hypochlorous acid or  $\text{Cl}_2\text{O}$ .

The most stable solid hypochlorites are those of Li, Ca, Sr and Ba (see below).  $\text{NaOCl}$  has only poor stability and cannot be isolated pure;  $\text{KOCl}$  is known only in solution, Mg yields a basic hypochlorite and impure Ag and Zn hypochlorites have been reported. Hydrated salts are also known. Solid, yellow, hydrated hypobromites  $\text{NaOBr} \cdot x\text{H}_2\text{O}$  ( $x = 5, 7$ ) and  $\text{KOB}r \cdot 3\text{H}_2\text{O}$  can be crystallized from solutions obtained by adding  $\text{Br}_2$  to cold conc solutions of MOH but the compounds decompose above  $0^\circ\text{C}$ . No solid metal hypoiodites have yet been isolated.

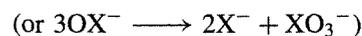
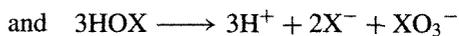
HOCl is more stable than HOBr and HOI and its microwave spectrum in the gas phase confirms the expected nonlinear geometry with H–O 97 pm, O–Cl 169.3 pm, and angle H–O–Cl  $103 \pm 3^\circ$  (cf. HOF, p. 857). All three

hypohalous acids are weak and solutions of their salts are therefore alkaline since the equilibrium



lies well to the right. Except at high pH, hypohalite solutions contain significant amounts of the undissociated acid. Approximate values for the acid dissociation constants  $K_a$  at room temperature are HOCl  $2.9 \times 10^{-8}$ , HOBr  $5 \times 10^{-9}$ , HOI  $\sim 10^{-11}$ ; these values are close to those of many  $\alpha$ -aminoacids and may also be compared with carbonic acid  $K_a$   $4.3 \times 10^{-7}$ , which is some 10 times stronger than HOCl, and phenol, which has  $K_a$   $1.3 \times 10^{-10}$ .

The manner and rate of decomposition of hypohalous acids (and hypohalite ions) in solution are much influenced by the concentration, pH and temperature of the solutions, by the presence or absence of salts which can act as catalysts, promoters or activators, and by light quanta. The main competing modes of decomposition are:



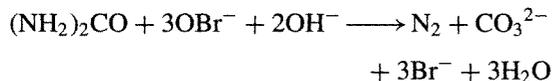
The acids decompose more readily than the anions so hypohalites are stabilized in basic solutions. The stability of the anions diminishes in the sequence  $\text{ClO}^- > \text{BrO}^- > \text{IO}^-$ .

Hypochlorites are amongst the strongest of the more common oxidizing agents and they react with inorganic species, usually by the net transfer of an O atom. Kinetic studies suggest that the oxidizing agent can be either HOCl or  $\text{OCl}^-$  in a given reaction, but rarely both simultaneously. Some typical examples are in Table 17.21. Hypochlorites react with ammonia and organic amino compounds to form chloramines. The characteristic "chlorine" odour of water that has been sterilized with hypochlorite is, in fact, due to chloramines produced from attack on bacteria. By contrast, hypobromites

**Table 17.21** Oxidation of inorganic substrates with HOCl or OCl<sup>-</sup>

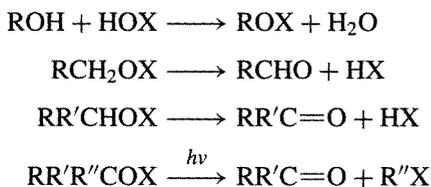
HOCl		OCl <sup>-</sup>	
Substrate	Products	Substrate	Products
HCO <sub>2</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	ClO <sup>-</sup>	ClO <sub>2</sub> <sup>-</sup>
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	CO <sub>2</sub>	ClO <sub>2</sub> <sup>-</sup>	ClO <sub>3</sub> <sup>-</sup>
OCN <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup> , N <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	CN <sup>-</sup>	OCN <sup>-</sup>
NH <sub>3</sub>	NCl <sub>3</sub>	NH <sub>3</sub>	NH <sub>2</sub> Cl
NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>
H <sub>2</sub> O <sub>2</sub>	O <sub>2</sub>	IO <sub>3</sub> <sup>-</sup>	IO <sub>4</sub> <sup>-</sup>
S	SO <sub>4</sub> <sup>2-</sup>	Mn <sup>2+</sup>	MnO <sub>4</sub> <sup>-</sup>
Br <sup>-</sup>	Br <sub>2</sub> (acid)	Br <sup>-</sup>	OBr <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> (alkaline)
I <sup>-</sup>	I <sub>2</sub> (acid)	I <sup>-</sup>	OI <sup>-</sup> , IO <sub>3</sub> <sup>-</sup> (alkaline)

oxidize amines quantitatively to N<sub>2</sub>, a reaction that is exploited in the analysis of urea:



Other uses of hypohalous acids and hypohalites are described in the Panel.

This section concludes with a reminder that, in addition to the hypohalous acids HOX and metal hypohalites M(OX)<sub>n</sub>, various covalent (molecular) hypohalites are known. Hypochlorites are summarized in Table 17.22. All are volatile liquids or gases at room temperature and are discussed elsewhere (see Index). Organic hypohalites are unstable and rapidly expel HX or RX to form the corresponding aldehyde or ketone:



*Halous acids, HOXO, and halites,*  
XO<sub>2</sub><sup>-</sup> (98,115,119,120)

Chlorous acid is the least stable of the oxoacids of chlorine; it cannot be isolated but is known in dilute aqueous solution. HOBrO and HOIO are even less stable, and, if they exist at all, have only a fleeting presence in aqueous solutions. Several chlorites have been isolated and NaClO<sub>2</sub> is sufficiently stable to be manufactured as an article of commerce on the kilotonne pa scale. Little reliable information is available on bromites and still less is established for iodites which are essentially non-existent.

HClO<sub>2</sub> is formed (together with HClO<sub>3</sub>) during the decomposition of aqueous solutions of ClO<sub>2</sub> (p. 847) but the best laboratory preparation is to treat an aqueous suspension of Ba(ClO<sub>2</sub>)<sub>2</sub> with

<sup>119</sup> G. GORDON, R. G. KIEFFER and D. H. ROSENBLATT, *Progr. Inorg. Chem.* **15**, 201–86 (1972). The first half of this review deals with the aqueous solution chemistry of chlorous acid and chlorites.

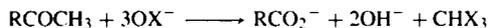
<sup>120</sup> F. SOLYMOSI, *Structure and Stability of Salts of the Halogen Oxyacids in the Solid Phase*, Wiley, UK, 1978, 468 pp.

**Table 17.22** Physical properties of some molecular hypochlorites

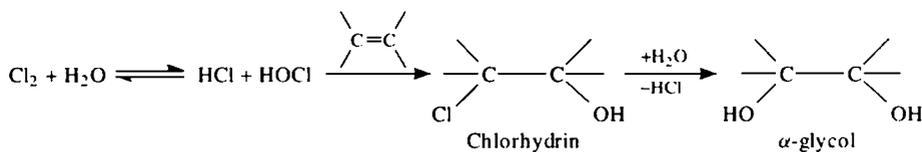
Compound	MP/°C	BP/°C	Compound	MP/°C	BP/°C
ClONO <sub>2</sub>	-107	18	ClOSeF <sub>5</sub>	-115	31.5
ClOClO <sub>3</sub>	-117	44.5	ClOTeF <sub>5</sub>	-121	38.5
ClOSO <sub>2</sub> F	-84.3	45.1	ClOOSF <sub>5</sub>	-130	26.4
ClOSF <sub>5</sub>	—	8.9	ClOOCF <sub>3</sub>	-132	-22

### Some Uses of Hypohalous Acids and Hypohalites

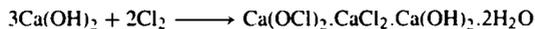
In addition to the applications indicated on p. 858, hypohalous acids are useful halogenating agents for both aromatic and aliphatic compounds. HOBr and HOI are usually generated *in situ*. The ease of aromatic halogenation increases in the sequence  $\text{OCl}^- < \text{OBr}^- < \text{OI}^-$  and is facilitated by salts of Pb or Ag. Another well-known reaction of hypohalites is their cleavage of methyl ketones to form carboxylates and haloform:



This is the basis of the iodoform test for the  $\text{CH}_3\text{CO}$  group. In addition to these reactions there is considerable industrial use for HOCl and hypochlorites in the manufacture of hydrazine (p. 427), chlorhydrins and  $\alpha$ -glycols:



By far the largest tonnage of hypochlorites is used for bleaching and sterilizing. "Liquid bleach" is an alkaline solution of NaOCl (pH  $\geq 11$ ); domestic bleaches have about 5% "available chlorine" content<sup>†</sup> whereas small-scale commercial installations such as laundries use  $\sim 12\%$  concentration. Chlorinated trisodium phosphate, which is a crystalline efflorescent product of approximate empirical composition  $(\text{Na}_3\text{PO}_4 \cdot 11\text{H}_2\text{O})_4 \cdot \text{NaOCl}$ , has 3.5–4.5% available Cl and is used in automatic dishwasher detergents, scouring powders, and acid metal cleaners for dairy equipment. Paper and pulp bleaching is effected by "bleach liquor", a solution of  $\text{Ca}(\text{OCl})_2$  and  $\text{CaCl}_2$ , yielding  $\sim 85 \text{ g l}^{-1}$  of "available chlorine". Powdered calcium hypochlorite,  $\text{Ca}(\text{OCl})_2 \cdot 2\text{H}_2\text{O}$  (70% available Cl), is used for swimming-pool sanitation whereas "bleaching powder",  $\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  (obtained by the action of  $\text{Cl}_2$  gas on slaked lime) contains 35% available Cl and is used for general bleaching and sanitation:



The speciality chemical LiOCl (40% "Cl") is used when calcium is contra-indicated, such as in the sanitation of hard water and in some dairy applications. Some idea of the scale of these applications can be gained from the following production figures which relate to the USA:<sup>(98)</sup>

LiOCl  $\sim 2500$  tonnes pa. Price (1993)  $\sim \$ 2.80/\text{kg}$ .

NaOCl  $\sim 250000$  tpa (on a dry basis) used mainly for household liquid bleach, laundries, disinfection of swimming pools, municipal water supplies and sewage, and the industrial manufacture of  $\text{N}_2\text{H}_4$  and organic chemicals.

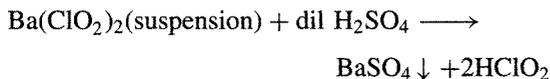
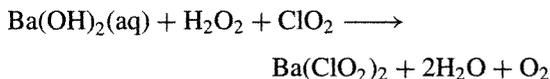
NaOCl  $(\text{Na}_3\text{PO}_4 \cdot 11\text{H}_2\text{O})_4$  was commercialized in 1930 and demand rose to 81000 tonnes in 1973. Use has dropped sharply since about 1980 (37000 tonnes in 1988, price  $\$ 0.70/\text{kg}$ ).

$\text{Ca}(\text{OCl})_2 \sim 85000$  tpa plus production facilities in numerous other countries (e.g. the USSR, Japan, South Africa and Canada).

Bleaching power is now much less used than formerly in highly industrialized countries but is still manufactured on a large scale in less-developed regions. In the USA its production peaked at 133000 tonnes in 1923 but had fallen to 23600 tonnes by 1955 and has not been reported since, though  $\sim 1160$  tonnes per annum were imported during the 1980s.

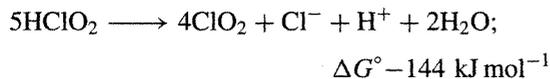
<sup>†</sup>"Available chlorine" content is defined as the weight of  $\text{Cl}_2$  which liberates the same amount of  $\text{I}_2$  from HI as does a given weight of the compound; it is often expressed as a percentage. For example, from the two (possibly hypothetical) stoichiometric equations  $\text{Cl}_2 + 2\text{HI} \rightarrow \text{I}_2 + 2\text{HCl}$  and  $\text{LiOCl} + 2\text{HI} \rightarrow \text{I}_2 + \text{LiCl} + \text{H}_2\text{O}$  it can be seen that 1 mol of  $\text{I}_2$  is liberated by 70.92 g  $\text{Cl}_2$  or by 58.4 g LiOCl. Whence the "available chlorine" content of pure LiOCl is  $(70.92/58.4) \times 100 = 121\%$ . The commercial product is usually diluted by sulfates to about one-third of this strength (see below).

dilute sulfuric acid:

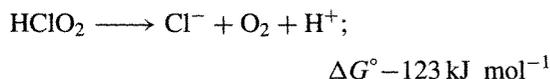
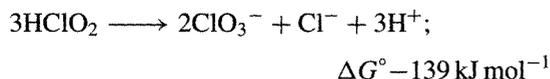


Evidence for the undissociated acid comes from spectroscopic data but the solutions cannot be concentrated without decomposition.  $\text{HClO}_2$  is a moderately strong acid  $K_a(25^\circ\text{C}) 1.1 \times 10^{-2}$  (cf  $\text{H}_2\text{SeO}_4 K_a 1.2 \times 10^{-2}$ ,  $\text{H}_4\text{P}_2\text{O}_7 K_a 2.6 \times 10^{-2}$ ).

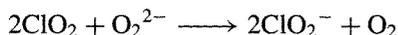
The decomposition of chlorous acid depends sensitively on its concentration, pH and the presence of catalytically active ions such as  $\text{Cl}^-$  which is itself produced during the decomposition. The main mode of decomposition (particularly if  $\text{Cl}^-$  is present) is to form  $\text{ClO}_2$ :



Competing modes produce  $\text{ClO}_3^-$  or evolve  $\text{O}_2$ :



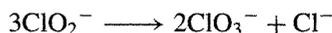
Metal chlorites are normally made by reduction of aqueous solutions of  $\text{ClO}_2$  in the presence of the metal hydroxide or carbonate. As with the preparation of  $\text{Ba(ClO}_2)_2$  above, the reducing agent is usually a peroxide since this adds no contaminant to the resulting chlorite solution:



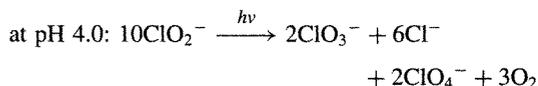
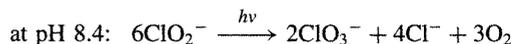
The  $\text{ClO}_2^-$  ion is nonlinear, as expected, and X-ray studies of  $\text{NH}_4\text{ClO}_2$  (at  $-35^\circ$ ) and of  $\text{AgClO}_2$  lead to the dimensions  $\text{Cl}-\text{O}$  156 pm, angle  $\text{O}-\text{Cl}-\text{O}$   $111^\circ$ . The chlorites of the alkali metals and alkaline earth metals are colourless or pale yellow. Heavy metal chlorites tend to explode or detonate when heated or struck (e.g. those of  $\text{Ag}^+$ ,  $\text{Hg}^+$ ,  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$  and also those of  $\text{Cu}^{2+}$  and  $\text{NH}_4^+$ ). Sodium chlorite is the only one to

have sufficient stability and to be sufficiently inexpensive to be a major article of commerce (see below).

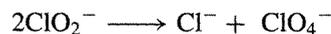
Anhydrous  $\text{NaClO}_2$  crystallizes from aqueous solutions above  $37.4^\circ$  but below this temperature the trihydrate is obtained. The commercial product contains about 80%  $\text{NaClO}_2$ . The anhydrous salt forms colourless deliquescent crystals which decompose when heated to  $175-200^\circ$ : the reaction is predominantly a disproportionation to  $\text{ClO}_3^-$  and  $\text{Cl}^-$  but about 5% of molecular  $\text{O}_2$  is also released (based on the  $\text{ClO}_2^-$  consumed). Neutral and alkaline aqueous solutions of  $\text{NaClO}_2$  are stable at room temperature (despite their thermodynamic instability towards disproportionation as evidenced by the reduction potentials on p. 854). This is a kinetic activation-energy effect and, when the solutions are heated near to boiling, slow disproportionation occurs:



Photochemical decomposition is rapid and the products obtained depend on the pH of the solution;



The stoichiometry in acid solution implies that, in addition to the more usual disproportionation into  $\text{ClO}_3^-$  and  $\text{Cl}^-$ , the following disproportionation also occurs:



The mechanisms of these various reactions have been the object of many studies.<sup>(98,115,119)</sup>

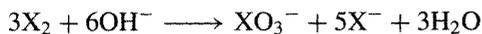
The main commercial applications of  $\text{NaClO}_2$  are in the bleaching and stripping of textiles, and as a source of  $\text{ClO}_2$  where required volumes are comparatively small. It is also used as an oxidant for removal of nitrogen oxide pollutants from industrial off-gases. The specific oxidizing properties of  $\text{NaClO}_2$  towards certain malodorous or toxic compounds such as unsaturated aldehydes, mercaptans, thioethers,

H<sub>2</sub>S and HCN have likewise led to its use for scrubbing the off-gases of processes where these noxious pollutants are formed. Production statistics are rather sparse but the main production plants are in Europe, which produced some 11 000 tonnes pa in 1990 and the USA, where production is expected to exceed 10 000 tpa in 1995. Other major producers are in Japan (~5000 tpa) and Canada (2700 tpa in 1990). The 1991 price for technical grade NaClO<sub>2</sub> in the USA was \$2.65/kg.

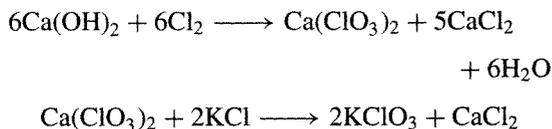
Crystalline barium bromite Ba(BrO<sub>2</sub>)<sub>2</sub>.H<sub>2</sub>O was first isolated in 1959; it can be made by treating the hypobromite with Br<sub>2</sub> at pH 11.2 and 0°C, followed by slow evaporation. Sr(BrO<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O was obtained similarly.

### *Halic acids, HOXO<sub>2</sub>, and halates, XO<sub>3</sub><sup>-</sup>* (121,122)

Disproportionation of X<sub>2</sub> in hot alkaline solution has long been used to synthesize chlorates and bromates (see oxidation state diagrams, p. 855):

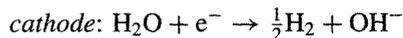
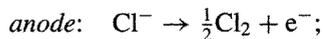


For example, J. von Liebig developed the technical preparation of KClO<sub>3</sub> by passing Cl<sub>2</sub> into a warm suspension of Ca(OH)<sub>2</sub> and then adding KCl to enable the less-soluble chlorate to crystallize on cooling:



However, only one-sixth of the halogen present is oxidized and alternative routes are more generally preferred for large-scale manufacture. Thus, the most important halate, NaClO<sub>3</sub>, is manufactured

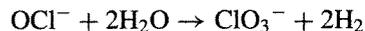
on a huge scale<sup>†</sup> by the electrolysis of brine in a diaphragmless cell which promotes efficient mixing. Under these conditions, the Cl<sub>2</sub> produced by anodic oxidation of Cl<sup>-</sup> reacts with cathodic OH<sup>-</sup> to give hypochlorite which then either disproportionates or is itself further anodically oxidized to ClO<sub>3</sub><sup>-</sup>:



*further disproportionation:*



*further anodic oxidation:*



Modern cells employ arrays of anodes (TiO<sub>2</sub> coated with a noble metal) and cathodes (mild steel) spaced 3 mm apart and carrying current at 2700 A m<sup>-2</sup> into brine (80–100 g l<sup>-1</sup>) at 60–80°C. Under these conditions current efficiency can reach 93% and 1 tonne of NaClO<sub>3</sub> can be obtained from 565 kg NaCl and 4535 kWh of electricity. The off-gas H<sub>2</sub> is also collected.

Bromates and iodates are prepared on a much smaller scale, usually by chemical oxidation. For example, Br<sup>-</sup> is oxidized to BrO<sub>3</sub><sup>-</sup> by aqueous hypochlorite (conveniently effected by passing

<sup>†</sup> World production of NaClO<sub>3</sub> (1989–91) exceeds 2 billion tonnes pa, Canada alone producing some 872 000 tpa, USA 630 000 tpa and Europe 421 000 tpa. Consumption in the USA exceeds production by some 50%, the rest being imported. The 1991 price (~\$480/tonne) was similar in both North America and Europe where, interestingly, the main consumers are Finland (156 800 tpa) and Sweden (109 700 tpa). The overwhelming use of NaClO<sub>3</sub> (95% in the USA) is in the manufacture of ClO<sub>2</sub>, mainly for bleaching paper pulp (p. 846). Other uses are to make perchlorates and other chlorates (3%), in uranium production (1% but declining sharply) and for agricultural uses (0.7%) such as herbicides, cotton defoliant and soya-bean desiccants. The use of NaClO<sub>3</sub> in pyrotechnic formulations is hampered by its hygroscopicity. KClO<sub>3</sub> does not suffer this disadvantage and is unexcelled as an oxidizer in fireworks and flares, the colours being obtained by admixture with salts of Sr (red), Ba (green), Cu (blue), etc. In addition KClO<sub>3</sub> is a crucial component in the head of "safety matches" (KClO<sub>3</sub>, S, Sb<sub>2</sub>S<sub>3</sub>, powdered glass and dextrin paste). Its price is very similar to that of NaClO<sub>3</sub>.

<sup>121</sup> Ref. 23, pp. 1418–35, Halic acids and halates.

<sup>122</sup> S. K. MENDIRATTA and B. L. DUNCAN, Chloric acid and chlorates, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 5, pp. 998–1016, Wiley, New York, 1993.

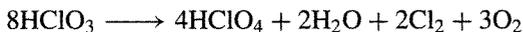
Cl<sub>2</sub> into alkaline solutions of Br<sup>-</sup>). Iodates can be prepared either by direct high-pressure oxidation of alkali metal iodides with oxygen at 600° or by oxidation of I<sub>2</sub> with chlorates:



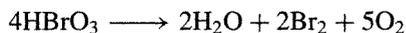
Salts of other metals are obtained by metathesis, and aqueous solutions of the corresponding acids are obtained by controlled addition of sulfuric acid to the barium salts:



Chloric acid, HClO<sub>3</sub>, is fairly stable in cold water up to about 30% concentration but, on being warmed, such solutions evolve Cl<sub>2</sub> and ClO<sub>2</sub>. Evaporation under reduced pressure can increase the concentration up to about 40% (~HClO<sub>3</sub>·7H<sub>2</sub>O) but thereafter it is accompanied by decomposition to HClO<sub>4</sub> and the evolution of Cl<sub>2</sub>, O<sub>2</sub> and ClO<sub>2</sub>:



Likewise, aqueous HBrO<sub>3</sub> can be concentrated under reduced pressure to about 50% concentration (~HBrO<sub>3</sub>·7H<sub>2</sub>O) before decomposition obtrudes:



Both chloric and bromic acids are strong acids in aqueous solution ( $\text{p}K_a \lesssim 0$ ) whereas iodic acid is slightly weaker, with  $\text{p}K_a$  0.804, i.e.  $K_a$  0.157.

Iodic acid is more conveniently synthesized by oxidation of an aqueous suspension of I<sub>2</sub> either electrolytically or with fuming HNO<sub>3</sub>. Crystallization from acid solution yields colourless, orthorhombic crystals of α-HIO<sub>3</sub> which feature H-bonded pyramidal molecules of HOIO<sub>2</sub>:  $r(\text{I}-\text{O})$  181 pm,  $r(\text{I}-\text{OH})$  189 pm, angle O-I-O 101.4°, angle O-I-(OH) 97°. When heated to ~100°C iodic acid partly dehydrates to HI<sub>3</sub>O<sub>8</sub> (p. 852); this comprises an H-bonded array of composition HOIO<sub>2</sub>·I<sub>2</sub>O<sub>5</sub> in which the HIO<sub>3</sub> has almost identical dimensions to those in α-HIO<sub>3</sub>. Further heating to 200° results in complete dehydration to I<sub>2</sub>O<sub>5</sub>. In concentrated aqueous solutions

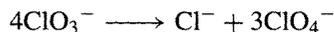
of HIO<sub>3</sub>, the iodate ions formed by deprotonation react with undissociated acid according to the equilibrium



Accordingly, crystallization of iodates from solutions containing an excess of HIO<sub>3</sub> sometimes results in the formation of hydrogen biiodates, M<sup>I</sup>H(IO<sub>3</sub>)<sub>2</sub>, or even dihydrogen triiodates, M<sup>I</sup>H<sub>2</sub>(IO<sub>3</sub>)<sub>3</sub>.

Chlorates and bromates feature the expected pyramidal ions XO<sub>3</sub><sup>-</sup> with angles close to the tetrahedral (106–107°). With iodates the interatomic angles at iodine are rather less (97–105°) and there are three short I–O distances (177–190 pm) and three somewhat longer distances (251–300 pm) leading to distorted perovskite structures (p. 963) with pseudo-sixfold coordination of iodine and piezoelectric properties (p. 58). In Sr(IO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O the coordination number of iodine rises to 7 and this increases still further to 8 (square antiprism) in Ce(IO<sub>3</sub>)<sub>4</sub> and Zr(IO<sub>3</sub>)<sub>4</sub>.

The modes of thermal decomposition of the halates and their complex oxidation-reduction chemistry reflect the interplay of both thermodynamic and kinetic factors. On the one hand, thermodynamically feasible reactions may be sluggish, whilst, on the other, traces of catalyst may radically alter the course of the reaction. In general, for a given cation, thermal stability decreases in the sequence iodate > chlorate > bromate, but the mode and ease of decomposition can be substantially modified. For example, alkali metal chlorates decompose by disproportionation when fused:

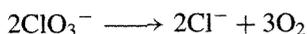


e.g. LiClO<sub>3</sub>, mp 125° (d 270°); NaClO<sub>3</sub>, mp 248° (d 265°); KClO<sub>3</sub>, mp 368° (d 400°).<sup>†</sup> However, in

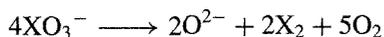
<sup>†</sup> Note, however, that thermal decomposition of NH<sub>4</sub>ClO<sub>3</sub> begins at 50°C and the compound explodes on further heating; this much lower decomposition temperature may result from prior proton transfer to give the less-stable acid: [NH<sub>4</sub>ClO<sub>3</sub> → NH<sub>3</sub> + HClO<sub>3</sub>].

A similar thermal instability afflicts NH<sub>4</sub>BrO<sub>3</sub> (d -5°) and NH<sub>4</sub>IO<sub>3</sub> (d ~ 100°).

the presence of a transition-metal catalyst such as  $\text{MnO}_2$  decomposition of  $\text{KClO}_3$  to  $\text{KCl}$  and oxygen begins at about  $70^\circ$  and is vigorous at  $100^\circ$



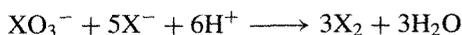
This is, indeed, a classic laboratory method for preparing small amounts of oxygen (p. 603). For bromates and iodates, disproportionation to halide and perchalate is not thermodynamically feasible and decomposition occurs either with formation of halide and liberation of  $\text{O}_2$  (as in the catalysed decomposition of  $\text{ClO}_3^-$  just considered), or by formation of the oxide:



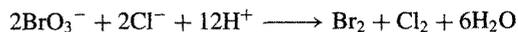
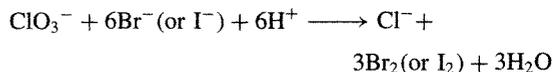
For all three halates (in the absence of disproportionation) the preferred mode of decomposition depends, again, on both thermodynamic and kinetic considerations. Oxide formation tends to be favoured by the presence of a strongly polarizing cation (e.g. magnesium, transition-metal and lanthanide halates), whereas halide formation is observed for alkali-metal, alkaline-earth and silver halates.

The oxidizing power of the halate ions in aqueous solution, as measured by their standard reduction potentials (p. 854), decreases in the sequence bromate  $\gtrsim$  chlorate  $>$  iodate but the rates of reaction follow the sequence iodate  $>$  bromate  $>$  chlorate. In addition, both the thermodynamic oxidizing power and the rate of reaction depend markedly on the hydrogen-ion concentration of the solution, being substantially greater in acid than in alkaline conditions (p. 855).

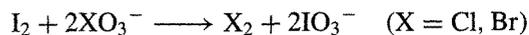
An important series of reactions, which illustrates the diversity of behaviour to be expected, is the comproportionation of halates and halides. Bromides are oxidized quantitatively to bromine and iodides to iodine, this latter reaction being much used in volumetric analysis:



Numerous variants are possible, e.g.:

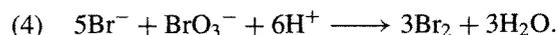
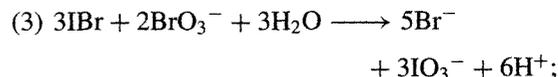


The greater thermodynamic stability of iodates enables iodine to displace  $\text{Cl}_2$  and  $\text{Br}_2$  from their halates:

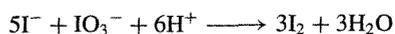


With bromate at pH 1.5–2.5 the reaction occurs in four stages:

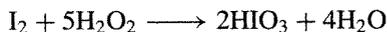
(1) an induction period in which a catalyst (probably  $\text{HOBr}$ ) is produced;



The dependence of reaction rates on pH and on the relative and absolute concentrations of reacting species, coupled with the possibility of autocatalysis and induction periods, has led to the discovery of some spectacular kinetic effects such as H. Landolt's "chemical clock" (1885): an acidified solution of  $\text{Na}_2\text{SO}_3$  is reacted with an excess of iodic acid solution in the presence of starch indicator — the induction period before the appearance of the deep-blue starch-iodine colour can be increased systematically from seconds to minutes by appropriate dilution of the solutions before mixing. With an excess of sulfite, free iodine may appear and then disappear as a single pulse due to the following sequence of reactions:



A true periodic reaction was discovered by W. C. Bray in 1921 and involves the reduction of iodic acid to  $I_2$  by  $H_2O_2$  followed by the reoxidation of  $I_2$  to  $HIO_3$ :



The net reaction is the disproportionation of  $H_2O_2$  to  $H_2O + \frac{1}{2}O_2$  and the starch indicator oscillates between deep blue and colourless as the iodine concentration pulsates.

Even more intriguing is the Belousov–Zhabotinskii class of oscillating reactions some of which can continue for hours. Such a reaction was first observed in 1959 by B. P. Belousov who noticed that, in stirred sulfuric acid solutions containing initially  $KBrO_3$ , cerium(IV) sulfate and malonic acid,  $CH_2(CO_2H)_2$ , the concentrations of  $Br^-$  and  $Ce^{4+}$  underwent repeated oscillations of major proportions (e.g. tenfold changes on a time-scale which was constant but which could be varied from a few seconds to a few minutes depending on concentrations and temperature). These observations were extended by A. M. Zhabotinskii in 1964 to the bromate oxidation of several other organic substrates containing a reactive methylene group catalysed either by  $Ce^{IV}/Ce^{III}$  or  $Mn^{III}/Mn^{II}$ . Not surprisingly these reactions have attracted considerable attention, but detailed studies of their mechanisms are beyond the scope of this chapter.<sup>(123–125)</sup>

The various reactions of bromates and iodates are summarized in the schemes on p. 866.<sup>(121)</sup>

The oxidation of halates to perhalates is considered further in the next section.

### Perhalic acid and perhalates

Because of their differing structures, chemical reactions and applications, perchloric acid and

the perchlorates are best considered separately from the various periodic acids and their salts; the curious history of perbromates also argues for their individual treatment.

### Perchloric acid and perchlorates<sup>(126–128)</sup>

The most stable compounds of chlorine are those in which the element is in either its lowest oxidation state (–I) or its highest (VII): accordingly perchlorates are the most stable oxo-compounds of chlorine (see oxidation-state diagram, (p. 855) and most are extremely stable both as solids and as solutions at room temperature. When heated they tend to decompose by loss of  $O_2$  (e.g.  $KClO_4$  above  $400^\circ$ ). Aqueous solutions of perchloric acid and perchlorates are not notable oxidizing agents at room temperature but when heated they become vigorous, even violent, oxidants. Considerable CAUTION should therefore be exercised when handling these materials, and it is crucial to avoid the presence of readily oxidizable organic (or inorganic) matter since this can initiate reactions of explosive intensity.

On an industrial scale, perchlorates are now invariably produced by the electrolytic oxidation of  $NaClO_3$  (see Panel, p. 867). Alternative routes have historical importance but are now only rarely used, even for small-scale laboratory syntheses.

Perchloric acid is best made by treating anhydrous  $NaClO_4$  or  $Ba(ClO_4)_2$  with concentrated HCl, filtering off the precipitated chloride and concentrating the filtrate by distillation. The azeotrope (p. 815) boils at  $203^\circ C$  and contains 71.6%  $HClO_4$  (i.e.  $HClO_4 \cdot 2H_2O$ ). The anhydrous acid is obtained by low-pressure distillation of the azeotrope ( $p < 1 \text{ mmHg} = 0.13 \text{ kPa}$ ) in an all-glass apparatus in the presence of fuming sulfuric acid. Commercially available perchloric acid is usually 60–62% ( $\sim 3.5H_2O$ ) or 70–72%

<sup>123</sup> R. J. FIELD, E. KÖRÖS and R. M. NOYES, *J. Am. Chem. Soc.* **94**, 8649–64 (1972).

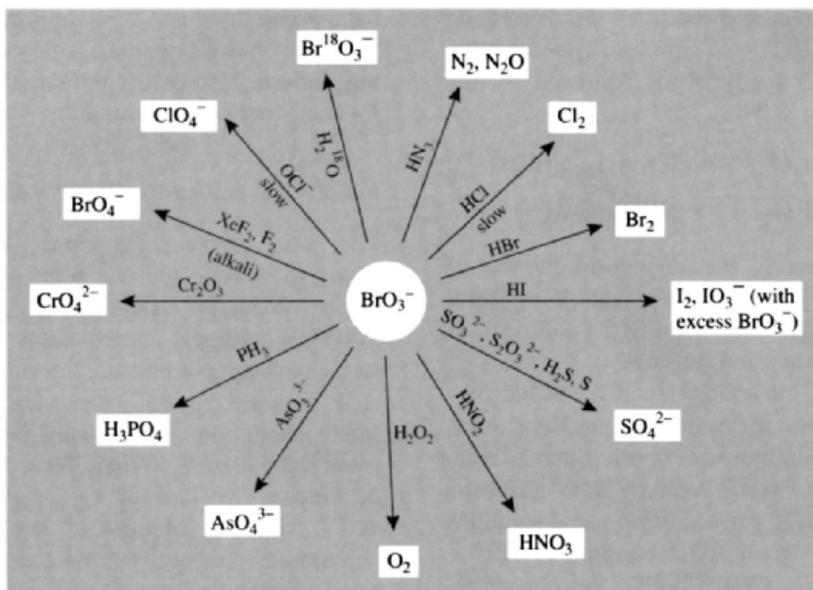
<sup>124</sup> R. M. NOYES, *J. Phys. Chem.* **94**, 4404–12 (1990).

<sup>125</sup> S. K. SCOTT, *Oscillations, Waves and Chaos in Chemical Kinetics*, Oxford Univ. Press, Oxford, 1994, 96 pp.

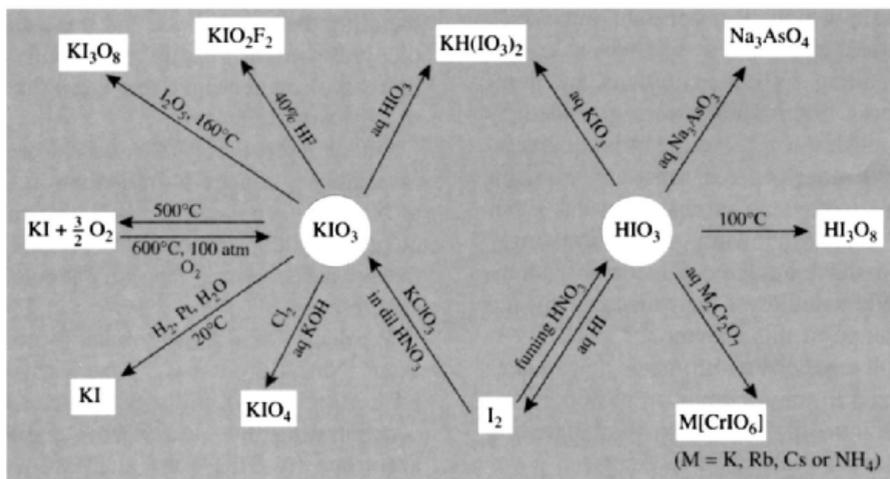
<sup>126</sup> Ref. 23, pp. 1435–60, Perhalic acids and perhalates.

<sup>127</sup> F. SOLYMOSI, *Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase*, Wiley, New York, 1978, 468 pp.

<sup>128</sup> A. A. SCHILT, *Perchloric Acid and Perchlorates*, Northern Illinois University Press, 1979, 189 pp.



Some reactions of aqueous bromates.



Some reactions of iodates.

( $\sim 2\text{H}_2\text{O}$ ); more concentrated solutions are hygroscopic and are also unstable towards loss of  $\text{Cl}_2\text{O}_7$  or violent decomposition by accidental impurities.

Pure  $\text{HClO}_4$  is a colourless mobile, shock-sensitive, liquid:  $d(25^\circ)$   $1.761\text{ g cm}^{-3}$ . At least 6 hydrates are known (Table 17.23). The structure of  $\text{HClO}_4$ , as determined by electron diffraction in the gas phase, is as shown in Fig. 17.20. This

molecular structure persists in the liquid phase, with some H bonding, and also in the crystalline phase, where an X-ray study at  $-160^\circ$  found three Cl–O distances of 142 pm and one of 161 pm<sup>(99)</sup> (very close to the dimensions of the extremely stable “isoelectronic” molecule,  $\text{FCIO}_3$  (140.4 and 161.9 pm, p. 879)). The (low) electrical conductivity and other physical properties of anhydrous  $\text{HClO}_4$  have been interpreted on the

### Production and Uses of Perchlorates

$\text{NaClO}_4$  is made by the electrolytic oxidation of aqueous  $\text{NaClO}_3$  using smooth Pt or  $\text{PbO}_2$  anodes and a steel cathode which also acts as the container. All other perchlorates, including  $\text{HClO}_4$ , are made either directly or indirectly from this  $\text{NaClO}_4$ . In a typical cell  $\text{NaClO}_3$  (600 g/l pH 6.5) is oxidized at 30–50°C with 90% current efficiency at 5000 A and 6.0 V with an anode current density of 3100  $\text{A m}^{-2}$  and an electrode separation of ~5 mm. The process can be either batch or continuous and energy consumption is ~2.5 kWh/kg. A small concentration of  $\text{Na}_2\text{Cr}_2\text{O}_7$  (1–5 g/l) is found to be extremely beneficial in inhibiting cathodic reduction of  $\text{ClO}_4^-$ .

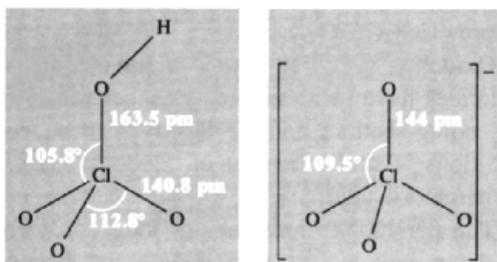
World production of perchlorates was less than 1800 tonnes pa until 1940 when wartime missile and rocket requirements boosted this tenfold. World production capacity peaked at around 40 000 tpa in 1963 but is now still above 30 000 tpa. More than half of this is converted to  $\text{NH}_4\text{ClO}_4$  for use as a propellant:



US production was severely disrupted by a series of devastating explosions in May 1988 which killed 2 people and injured several hundred.<sup>(129)</sup> Ultrapure  $\text{NH}_4\text{ClO}_4$  for physical measurements and research purposes can be made by direct neutralization of aqueous solutions of  $\text{NH}_3$  and  $\text{HClO}_4$ . One of the main current uses of  $\text{NH}_4\text{ClO}_4$  is in the Space Shuttle Programme: the two booster rockets use a solid propellant containing 70% by weight of  $\text{NH}_4\text{ClO}_4$ , this being the oxidizer for the “fuel” (powdered Al metal) which comprises most of the rest of the weight. Each shuttle launch requires about 770 tonnes of  $\text{NH}_4\text{ClO}_4$ .

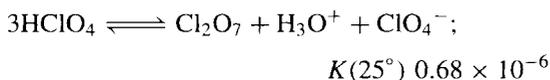
The annual consumption of 70%  $\text{HClO}_4$  is about 450 tonnes mainly for making other perchlorates. Most of the  $\text{NaClO}_4$  produced is used captively to make  $\text{NH}_4\text{ClO}_4$  and  $\text{HClO}_4$ , but about 725 tpa is used for explosives, particularly in slurry blasting formulations.

The two other perchlorates manufactured on a fairly large scale industrially are  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{KClO}_4$ . The former is used as the electrolyte in “dry cells” (batteries), whereas  $\text{KClO}_4$  is a major constituent in pyrotechnic devices such as fireworks, flares, etc. Thus the white flash and thundering boom in fireworks displays are achieved by incorporating a compartment containing  $\text{KClO}_4/\text{S}/\text{Al}$ , whereas the flash powder commonly used in rock concerts and theatricals comprises  $\text{KClO}_4/\text{Mg}$ . Vivid blues, perhaps the most difficult pyrotechnic colour to achieve, are best obtained from the low temperature (< 1200° C) flame emission of  $\text{CuCl}$  in the 420–460 nm region: because of the instability of copper chlorate and perchlorate this colour is generated by ignition of a mixture containing 38%  $\text{KClO}_3$ , 29%  $\text{NH}_4\text{ClO}_3$ , and 14%  $\text{CuCO}_3$  bound with red gum (14%) and dextrin (5%).



**Figure 17.20** Structure of the gaseous molecule  $\text{HClO}_4$  and of the  $\text{ClO}_4^-$  anion.

basis of slight dissociation according to the overall equilibrium:



(cf.  $\text{H}_2\text{SO}_4$ , p. 711;  $\text{H}_3\text{PO}_4$ , p. 518, etc.). The monohydrate forms an H-bonded crystalline lattice  $[\text{H}_3\text{O}]^+[\text{ClO}_4]^-$  that undergoes a phase transition with rotational disorder above  $-30^\circ$ ; it melts to a viscous, highly ionized liquid at  $49.9^\circ$ . The other hydrates also feature hydroxonium ions  $[(\text{H}_2\text{O})_n\text{H}]^+$  as described more fully on p. 630. It is particularly notable that hydration does not increase the coordination number of Cl and in this perchloric acid differs markedly from periodic acid (p. 872). This parallels the difference between sulfuric and telluric acids in the preceding group (p. 782).

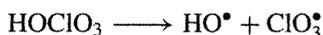
Anhydrous  $\text{HClO}_4$  is an extremely powerful oxidizing agent. It reacts explosively with most organic materials, ignites HI and  $\text{SOCl}_2$  and rapidly oxidizes Ag and Au. Thermal decomposition in the gas phase yields a mixture of  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$  and  $\text{O}_2$  depending on the conditions. Above  $310^\circ$  the decomposition is first

<sup>129</sup> R. J. SELTZER, *Chem. & Eng. News*, August 8, 7–15 (1988).

Table 17.23 Perchloric acid and its hydrates

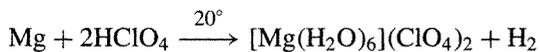
$n$ in $\text{HClO}_4 \cdot n\text{H}_2\text{O}$	Structure	MP/°C	BP/°C	$\Delta H_f^\circ/\text{kJ mol}^{-1}$
0	$\text{HOClO}_3$	-112	110 (expl)	-40.6 (liq)
0.25	$(\text{HClO}_4)_4 \cdot \text{H}_2\text{O}$	d-73.1	—	—
1	$[\text{H}_3\text{O}]^+[\text{ClO}_4]^-$	49.9	decomp	-382.2 (cryst)
2	$[\text{H}_5\text{O}_2]^+[\text{ClO}_4]^-$	-20.7	203	-688 (liq)
2.5	—	-33.1	—	—
3	$[\text{H}_7\text{O}_3]^+[\text{ClO}_4]^-$	-40.2	—	—
3.5	—	-45.9	—	—

order and homogeneous, the rate-determining step being homolytic fission of the Cl–OH bond:



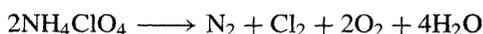
The hydroxyl radical rapidly abstracts an H atom from a second molecule of  $\text{HClO}_4$  to give  $\text{H}_2\text{O}$  plus  $\text{ClO}_4^\bullet$  and the 2 radicals  $\text{ClO}_3^\bullet$  and  $\text{ClO}_4^\bullet$  then decompose to the elements via the intermediate oxides. Above  $450^\circ$  the  $\text{Cl}_2$  produced reacts with  $\text{H}_2\text{O}$  to give  $2\text{HCl}$  plus  $\frac{1}{2}\text{O}_2$  whilst in the low-temperature range ( $150\text{--}310^\circ$ ) the decomposition is heterogeneous and second order in  $\text{HClO}_4$ .

Aqueous perchloric acid solutions exhibit very little oxidizing power at room temperature, presumably because of kinetic activation barriers, though some strongly reducing species slowly react, e.g.  $\text{Sn}^{\text{II}}$ ,  $\text{Ti}^{\text{III}}$ ,  $\text{V}^{\text{II}}$  and  $\text{V}^{\text{III}}$ , and dithionite. Others do not, e.g.  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{HNO}_2$ ,  $\text{HI}$  and, surprisingly,  $\text{Cr}^{\text{II}}$  and  $\text{Eu}^{\text{II}}$ . Electropositive metals dissolve with liberation of  $\text{H}_2$  and oxides of less basic metals also yield perchlorates. e.g. with 72% acid:



$\text{NO}$  and  $\text{NO}_2$  react to give  $\text{NO}^+\text{ClO}_4^-$  and  $\text{F}_2$  yields  $\text{FOClO}_3$  (p. 639).  $\text{P}_2\text{O}_5$  dehydrates the acid to  $\text{Cl}_2\text{O}_7$  (p. 850).

Perchlorates are known for most metals in the periodic table.<sup>(128)</sup> The alkali-metal perchlorates are thermally stable to several hundred degrees above room temperature but  $\text{NH}_4\text{ClO}_4$  deflagrates with a yellow flame when heated to  $200^\circ$ :



$\text{NH}_4\text{ClO}_4$  has a solubility in water of 20.2 g per 100 g solution at  $25^\circ$  and 135 g per 100 g liquid  $\text{NH}_3$  at the same temperature. Aqueous solubilities decrease in the sequence  $\text{Na} > \text{Li} > \text{NH}_4 > \text{K} > \text{Rb} > \text{Cs}$ ; indeed, the low solubility of the last 3 perchlorates in this series has been used for separatory purposes and even for gravimetric analysis (e.g.  $\text{KClO}_4$  1.99 g per 100 g  $\text{H}_2\text{O}$  at  $20^\circ$ ). Many of these perchlorates and those of  $\text{M}^{\text{II}}$  can also be obtained as hydrates.  $\text{AgClO}_4$  has the astonishing solubility of 557 g per 100 g  $\text{H}_2\text{O}$  at  $25^\circ$  and even in toluene its solubility is 101 g per 100 g  $\text{PhMe}$  at  $25^\circ$ . This has great advantages in the metathetic preparation of other perchlorates, particularly organic perchlorates, e.g.  $\text{RI}$  yields  $\text{ROClO}_3$ ,  $\text{Ph}_3\text{CCl}$  yields  $\text{Ph}_3\text{C}^+\text{ClO}_4^-$ , and  $\text{CCl}_4$  affords  $\text{CCl}_3\text{OCIO}_3$ .

Oxidation-reduction reactions involving perchlorates have been mentioned in several of the preceding sections and the reactivity of aqueous solutions is similar to that of aqueous solutions of perchloric acid.

The perchlorate ion was for long considered to be a non-coordinating ligand and has frequently been used to prepare “inert” ionic solutions of constant ionic strength for physicochemical measurements. Though it is true that  $\text{ClO}_4^-$  is a weaker ligand than  $\text{H}_2\text{O}$  it is not entirely toothless and, as shown schematically in Fig. 17.21, examples are known in which the perchlorate acts as a monodentate ( $\eta^1$ ), bidentate chelating ( $\eta^2$ ) and bidentate bridging ( $\mu, \eta^2$ ) ligand. The first unambiguous structural evidence for coordinated  $\text{ClO}_4^-$  was obtained in 1965 for the 5 coordinate cobalt(II)

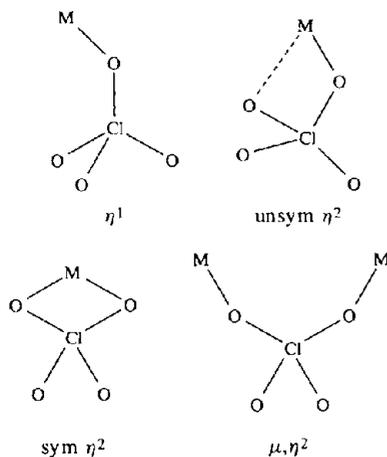


Figure 17.21 Coordination modes of  $\text{ClO}_4^-$  as determined by X-ray crystallography.

complex  $[\text{Co}(\text{OAsMePh}_2)_4(\eta^1\text{-OCIO}_3)_2]^{(130)}$  and this was quickly followed by a second example, the red 6-coordinate *trans* complex  $[\text{Co}(\eta^2\text{-MeSCH}_2\text{CH}_2\text{SMe})_2(\eta^1\text{-OCIO}_3)_2]^{(131)}$ . The two structures are shown in Fig. 17.22. The perchlorate ion has now been established as a monodentate ligand towards an s-block element (Ba),<sup>(132)</sup>

<sup>130</sup> P. PAULING, G. B. ROBERTSON and G. A. RODLEY, *Nature* **207**, 73–74 (1965).

<sup>131</sup> F. A. COTTON and D. L. WEAVER, *J. Am. Chem. Soc.* **87**, 4189–90 (1965).

<sup>132</sup> D. L. HUGHES, C. L. MORTIMER and M. R. TRUTER, *Acta Cryst.* **B34**, 800–7 (1978). *Inorg. Chim. Acta* **29**, 43–55 (1978).

a p-block element ( $\text{Sn}^{\text{II}}$  and  $\text{Sn}^{\text{IV}}$ ),<sup>(133)</sup> and an f-block element ( $\text{Sm}^{\text{III}}$ )<sup>(134)</sup> as well as to the d-block elements  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Ag}^{\text{I}}$ .<sup>(131,135)</sup> It is also known to function as a bidentate ligand towards Na,<sup>(136)</sup> Ba,<sup>(132)</sup>  $\text{Sn}^{\text{IV}}$ ,<sup>(133)</sup>  $\text{Sm}^{\text{III}}$ ,<sup>(134)</sup>  $\text{Ti}^{\text{IV}}$  in  $[\text{Ti}(\eta^2\text{-ClO}_4)_4]^{(137)}$  and  $\text{Ni}^{\text{II}}$  in  $[\text{Ni}(\eta^2\text{-ClO}_4)_2\text{L}_2]^+$  where L is a chiral bidentate organic ligand.<sup>(138)</sup> Sometimes both  $\eta^1$  and  $\eta^2$  modes occur in the same compound. The bidentate bridging mode occurs in the silver complex  $[\text{Ag}\{\mu, \eta^2\text{-OCl}(\text{O})_2\text{O}\}(m\text{-xylene})_2]^{(139)}$ . The structure of appropriate segments of some of these compounds are in Fig. 17.23. The distinction between coordinated and non-coordinated (“ionic”) perchlorate is sometimes hard to make and there is an almost continuous

<sup>133</sup> R. C. ELDER, M. J. HEEG and E. DEUTSCH, *Inorg. Chem.* **17**, 427–31 (1978). C. BELIN, M. CHAABOUNI, J.-L. PASCAL, J. POTIER and J. ROZIERE, *J. Chem. Soc., Chem. Commun.*, 105–6 (1980).

<sup>134</sup> M. CIAMPOLINI, N. NARDI, R. CINI, S. MANGANI and P. ORIOLI, *J. Chem. Soc., Dalton Trans.*, 1983–6 (1979).

<sup>135</sup> F. MADAULE-AUBRY and G. M. BROWN, *Acta Cryst.* **B24**, 745–53 (1968). F. BIGOLI, M. A. PELLINGHELLI and A. TIRIPICCHIO, *Cryst. Struct. Comm.* **4**, 123–6 (1976). E. A. HALL GRIFFITH and E. L. AMMA, *J. Am. Chem. Soc.* **93**, 3167–72 (1971).

<sup>136</sup> H. MILBURN, M. R. TRUTER and B. L. VICKERY, *J. Chem. Soc., Dalton Trans.*, 841–6 (1974).

<sup>137</sup> M. FOURATI, M. CHAABOUNI, C. H. BELIN, M. CHARBONNEL, J.-L. PASCAL and J. POTIER, *Inorg. Chem.* **25**, 1386–90 (1986).

<sup>138</sup> D. A. HOUSE, P. J. STEEL and A. A. WATSON, *J. Chem. Soc., Chem. Commun.*, 1575–6 (1987).

<sup>139</sup> I. F. TAYLOR, E. A. HALL and E. L. AMMA, *J. Am. Chem. Soc.* **91**, 5745–9 (1969).

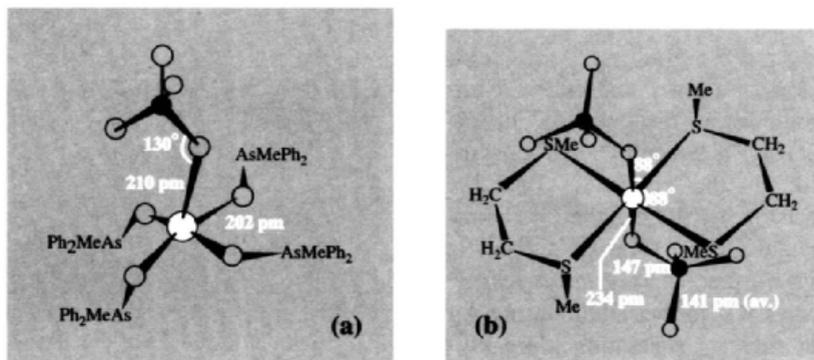


Figure 17.22 The structures of monodentate perchlorate complexes (see text).

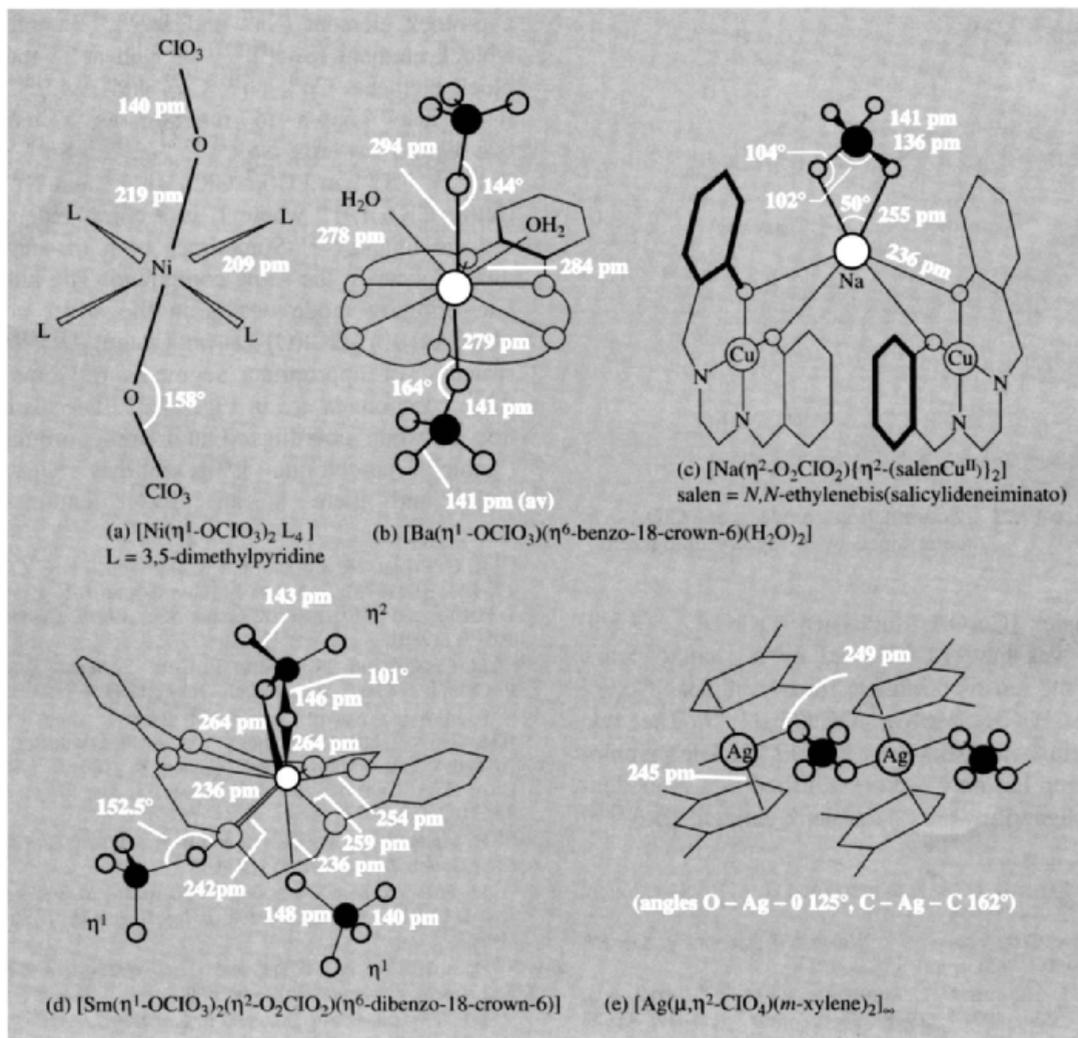
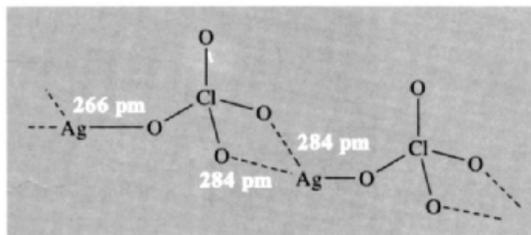


Figure 17.23 Examples of monodentate, chelating and bridging perchlorate ligands.

gradation between the two extremes. Similarly it is sometimes difficult to distinguish unambiguously between  $\eta^1$  and unsymmetrical  $\eta^2$  and, in the colourless complex  $[\text{Ag}(\text{cyclohexylbenzene})_2(\text{ClO}_4)]$ , the  $\eta^1$  bonding between Ag and  $\text{OCIO}_3$  (Ag–O 266 pm) is accompanied by a further weak symmetrical  $\eta^2$  bonding from each  $\text{ClO}_4$  to the neighbouring Ag (2Ag–O 284 pm) thereby generating a weakly-bridged chain-like structure involving pseudo- $\eta^3$  coordination of the perchlorate group.<sup>(135)</sup>



Because of its generally rather weak coordinating ability quite small changes can determine whether

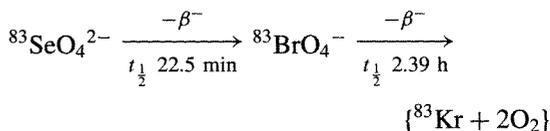
or not a perchlorate group coordinates and if so, in which mode. For example, the barium crown-ether dihydrate complex illustrated in Fig. 17.23 features 10-coordinate Ba with 6 oxygen atoms from the crown ring (Ba–O 280–285 pm), two H<sub>2</sub>O molecules (Ba–O 278 and 284 pm), and one of the perchlorates (Ba–O 294 pm) all on one side of the ring, and the other perchlorate (Ba–O 279 pm) below it. By contrast, the analogous strontium complex is a trihydrate with 9-coordinate Sr (six Sr–O from the crown ring at 266–272 pm, plus two H<sub>2</sub>O at 257, 259 pm, on one side of the ring, and one H<sub>2</sub>O on the other side at 255 pm); the ClO<sub>4</sub><sup>−</sup> ions are uncoordinated though they are H-bonded to the water molecules.

An even more dramatic change occurs with nickel(II) perchlorate complexes. Thus, the complex with 4 molecules of 3,5-dimethylpyridine (Fig. 17.23a) is blue, paramagnetic, and 6-coordinate with *trans*-(η<sup>1</sup>-OCIO<sub>3</sub>) ligands, whereas the corresponding complex with 3,4-dimethylpyridine is yellow and diamagnetic with square-planar Ni<sup>II</sup> and uncoordinated ClO<sub>4</sub><sup>−</sup> ions.<sup>(135,140)</sup> There is no steric feature of the structure which prevents the four 3,4-ligands from adopting the propeller-like configuration of the four 3,5-ligands thereby enabling Ni to accept two η<sup>1</sup>-OCIO<sub>3</sub>, or vice versa, and one must conclude that subtle differences in secondary valency forces and energies of packing are sufficient to dictate whether the complex that crystallizes is blue, paramagnetic and octahedral, or yellow, diamagnetic and square planar.

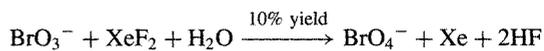
### Perbromic acid and perbromates

The quest for perbromic acid and perbromates and the various reasons adduced for their apparent non-existence make fascinating and salutary reading.<sup>(116)</sup> The esoteric radiochemical synthesis of BrO<sub>4</sub><sup>−</sup> in 1968 using the β-decay of radioactive <sup>83</sup>Se, whilst not providing a viable route to macroscopic quantities of perbromate,

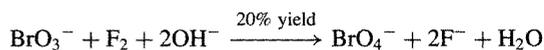
proved that this previously elusive species could exist:



This stimulated the search for a chemical synthesis. Electrolytic oxidation of aqueous LiBrO<sub>3</sub> produced a 1% yield of perbromate, but the first isolation of a solid perbromate salt (RbBrO<sub>4</sub>) was achieved by oxidation of BrO<sub>3</sub><sup>−</sup> with aqueous XeF<sub>2</sub>.<sup>(141)</sup>



The best synthesis is now by oxidation of alkaline solutions of BrO<sub>3</sub><sup>−</sup> using F<sub>2</sub> gas under rather specific conditions:<sup>(142)</sup>



In practice, F<sub>2</sub> is bubbled in until the solution is neutral, at which point excess bromate and fluoride are precipitated as AgBrO<sub>3</sub> and CaF<sub>2</sub>; the solution is then passed through a cation exchange column to yield a dilute solution of HBrO<sub>4</sub>. Several hundred grams at a time can be made by this route. The acid can be concentrated up to 6 M (55%) without decomposition and such solutions are stable for prolonged periods even at 100°. More concentrated solutions of HBrO<sub>4</sub> can be obtained but they are unstable; a white solid, possibly HBrO<sub>4</sub>·2H<sub>2</sub>O, can be crystallized.

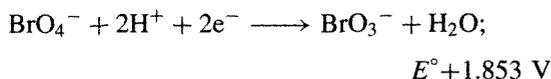
Pure KBrO<sub>4</sub> is isomorphous with KClO<sub>4</sub> and contains tetrahedral BrO<sub>4</sub><sup>−</sup> anions (Br–O 161 pm, cf. Cl–O 144 pm in ClO<sub>4</sub><sup>−</sup> and I–O 179 pm in IO<sub>4</sub><sup>−</sup>). Oxygen-18 exchange between 0.14 M KBrO<sub>4</sub> and H<sub>2</sub>O proceeds to less than 7% completion during 19 days at 94° in either acid or basic solutions and there is no sign of any increase in coordination number of Br; in this BrO<sub>4</sub><sup>−</sup> resembles ClO<sub>4</sub><sup>−</sup> rather than IO<sub>4</sub><sup>−</sup>. KBrO<sub>4</sub> is stable to 275–280° at which

<sup>140</sup> F. MADAULE-AUBRY, W. R. BUSING and G. M. BROWN, *Acta Cryst.* **B24**, 754–60 (1968).

<sup>141</sup> E. H. APPELMAN, *J. Am. Chem. Soc.* **90**, 1900–1 (1968); *Inorg. Chem.* **8**, 223–7 (1969).

<sup>142</sup> E. H. APPELMAN, *Inorg. Synth.* **13**, 1–9 (1972).

temperature it begins to dissociate into  $\text{KBrO}_3$  and  $\text{O}_2$ . Even  $\text{NH}_4\text{BrO}_4$  is stable to  $170^\circ$ . Dilute solutions of  $\text{BrO}_4^-$  show little oxidizing power at  $25^\circ$ ; they slowly oxidize  $\text{I}^-$  and  $\text{Br}^-$  but not  $\text{Cl}^-$ . More concentrated  $\text{HBrO}_4$  (3 M) readily oxidizes stainless steel and 12 M acid rapidly oxidizes  $\text{Cl}^-$ . The general inertness of  $\text{BrO}_4^-$  at room temperature stands in sharp contrast to its high thermodynamic oxidizing power, which is greater than that of any other oxohalogen ion that persists in aqueous solution. The oxidation potential is



(cf. 1.201 V for  $\text{ClO}_4^-$  and 1.653 for  $\text{IO}_4^-$ ). Accordingly, only the strongest oxidants would be expected to convert bromates to perbromates. As seen above,  $\text{F}_2/\text{H}_2\text{O}$  ( $E^\circ \sim 2.87 \text{ V}$ ) and  $\text{XeF}_2/\text{H}_2\text{O}$  ( $E^\circ \sim 2.64 \text{ V}$ ) are effective, but ozone ( $E^\circ 2.07 \text{ V}$ ) and  $\text{S}_2\text{O}_8^{2-}$  ( $E^\circ 2.01 \text{ V}$ ) are not, presumably for kinetic reasons. Thermochemical measurements<sup>(143)</sup> further show that  $\text{KBrO}_4$  is thermodynamically stable with respect to its elements, but less so than the corresponding  $\text{KClO}_4$  and  $\text{KIO}_4$ : this is not due to any significant difference in entropy effects or lattice energies and implies that the Br–O bond in  $\text{BrO}_4^-$  is substantially weaker than the X–O bond in the other perhalates. Some comparative data (298.15 K) are:

	$\text{KClO}_4$	$\text{KBrO}_4$	$\text{KIO}_4$
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	–431.9	–287.6	–460.6
$\Delta G_f^\circ/\text{kJ mol}^{-1}$	–302.1	–174.1	–349.3

No entirely satisfactory explanation of these observations has been devised, though they are paralleled by the similar reluctance of other elements following the completion of the 3d subshell to achieve their highest oxidation states — see particularly Se (p. 755) and As (p. 552) immediately preceding Br in the periodic table. The detailed kinetics of several oxidation reactions involving aqueous solutions of  $\text{BrO}_4^-$

have been studied.<sup>(144)</sup> In general, the reactivity of perbromates lies between that of the chlorates and perchlorates which means that, after the perchlorates, perbromates are the least reactive of the known oxohalogen compounds. It has even been suggested<sup>(116)</sup> that earlier investigators may actually have made perbromates, but not realized this because they were expecting a highly reactive product rather than an inert one.

### Periodic acids and periodates<sup>(126)</sup>

At least four series of periodates are known, interconnected in aqueous solutions by a complex series of equilibria involving deprotonation, dehydration and aggregation of the parent acid  $\text{H}_5\text{IO}_6$  — cf. telluric acids (p. 782) and antimonic acids (p. 577) in the immediately preceding groups. Nomenclature is summarized in Table 17.24, though not all of the fully protonated acids have been isolated in the free state. The structural relationship between these acids, obtained mainly from X-ray studies on their salts, are shown in Fig. 17.24.  $\text{H}_5\text{IO}_6$  itself (mp  $128.5^\circ$  decomp) consists of molecules of  $(\text{HO})_5\text{IO}$  linked into a three-dimensional array by  $\text{O} \cdots \text{H} \cdots \text{O}$  bonds (10 for each molecule, 260–278 pm).

Periodates can be made by oxidation of  $\text{I}^-$ ,  $\text{I}_2$  or  $\text{IO}_3^-$  in aqueous solution. Industrial processes involve oxidation of alkaline  $\text{NaIO}_3$  either electrochemically (using a  $\text{PbO}_2$  anode) or with  $\text{Cl}_2$ :



Table 17.24 Nomenclature of periodic acids

Formula	Name	Alternative	Formal relation to $\text{H}_5\text{IO}_6$
$\text{H}_5\text{IO}_6$	Orthoperiodic	Paraperiodic	Parent
$\text{HIO}_4$	Periodic	Metaperiodic	$\text{H}_5\text{IO}_6 - 2\text{H}_2\text{O}$
" $\text{H}_3\text{IO}_5$ "	Mesoperiodic	Diperiodic	$\begin{cases} 2\text{H}_5\text{IO}_6 - 2\text{H}_2\text{O} \\ 2\text{H}_3\text{IO}_5 - 3\text{H}_2\text{O} \end{cases}$
$\text{H}_7\text{I}_3\text{O}_{14}$	Triperiodic		$3\text{H}_5\text{IO}_6 - 4\text{H}_2\text{O}$

<sup>143</sup> F. SCHREINER, D. W. OSBORNE, A. V. POCIUS and E. H. APPELMAN, *Inorg. Chem.* **9**, 2320–4 (1970).

<sup>144</sup> E. H. APPELMAN, U. K. KLÄNING and R. C. THOMPSON, *J. Am. Chem. Soc.* **101**, 929–34 (1979).

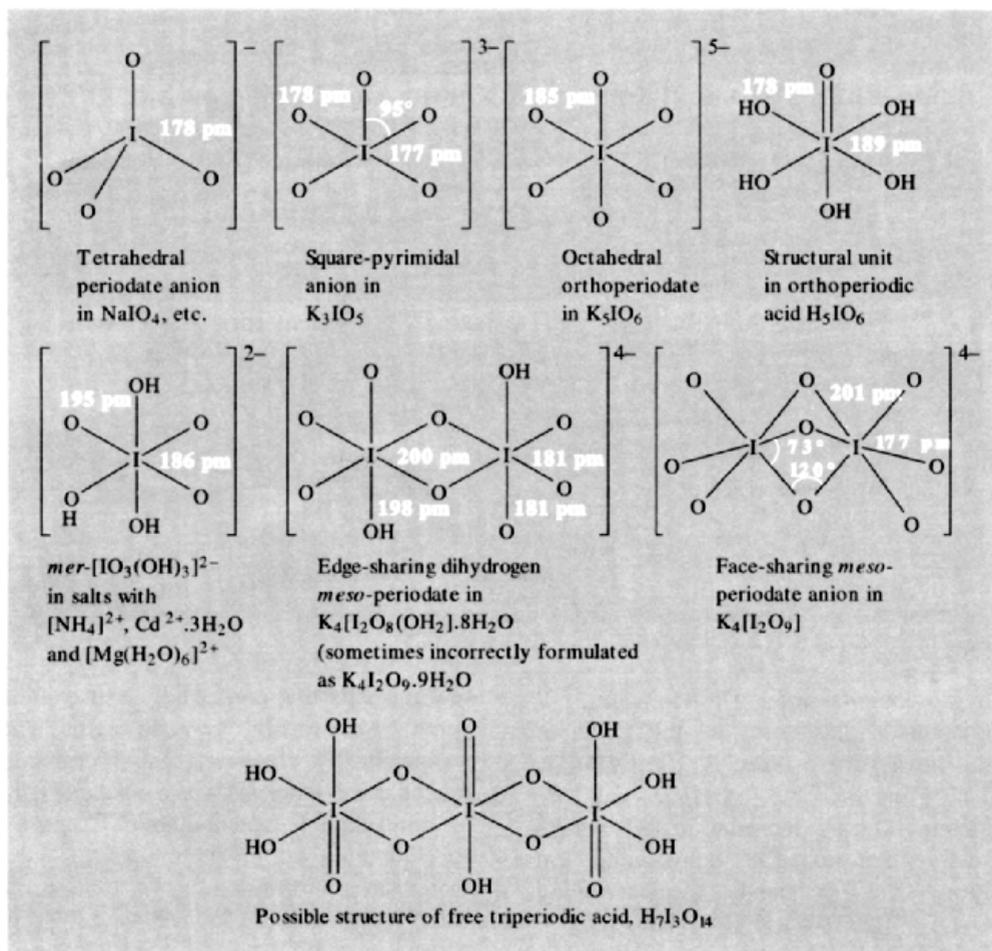
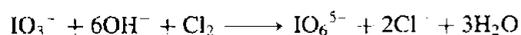
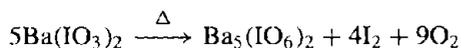


Figure 17.24 Structures of periodic acids and periodate anions.

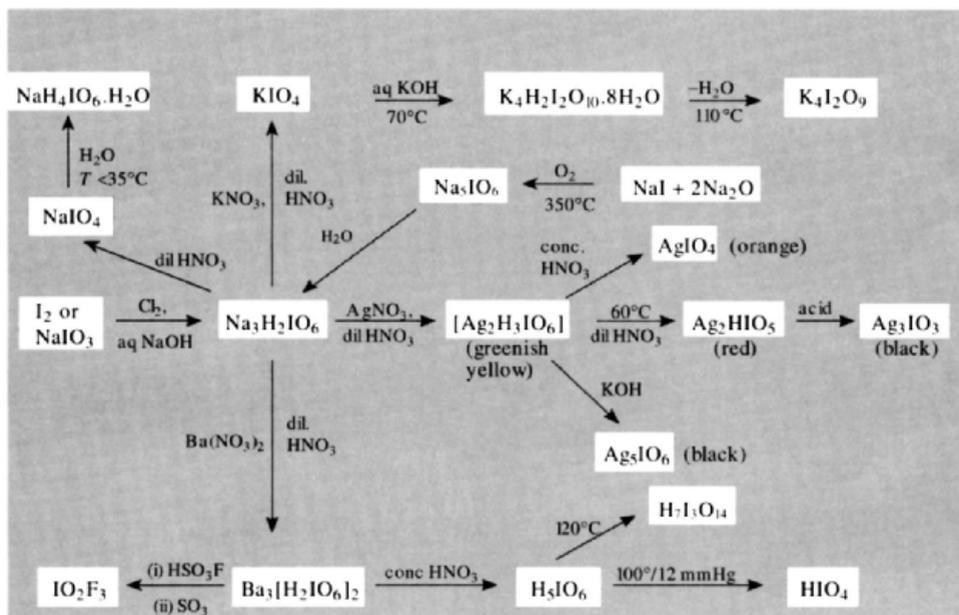


The product is the dihydrogen orthoperiodate  $\text{Na}_3\text{H}_2\text{IO}_6$ , which is a convenient starting point for many further preparations (see Scheme on next page). Paraperiodates of the alkaline earth metals can be made by the thermal disproportionation of the corresponding iodates, e.g.:



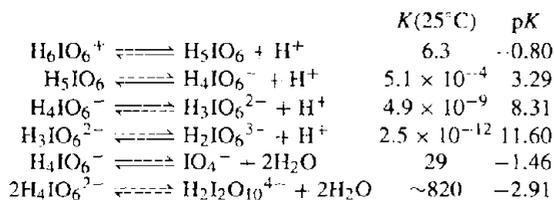
Aqueous solutions of periodic acid are best made by treating this barium salt with concentrated nitric acid. White crystals of

$\text{H}_5\text{IO}_6$  can be obtained from these solutions. Dehydration of  $\text{H}_5\text{IO}_6$  at  $120^\circ$  yields  $\text{H}_7\text{I}_3\text{O}_{14}$ , whereas heating to  $100^\circ$  under reduced pressure affords  $\text{HIO}_4$ . Attempts to dehydrate further do not yield the non-existent  $\text{I}_2\text{O}_7$  (p. 852); oxygen is progressively evolved to form the mixed oxide  $\text{I}_2\text{O}_5 \cdot \text{I}_2\text{O}_7$  and finally  $\text{I}_2\text{O}_5$ . Protonation of orthoperiodic acid with concentrated  $\text{HClO}_4$  yields the cation  $[\text{I}(\text{OH})_6]^+$ . Similarly, dissolution of crystalline  $\text{H}_5\text{IO}_6$  in 95%  $\text{H}_2\text{SO}_4$  (or  $\text{H}_2\text{SeO}_4$ ) at  $120^\circ$  yields colourless crystals of  $[\text{I}(\text{OH})_6][\text{HSO}_4]$  on slow cooling to room temperature and prolonged digestion of these with trichloroacetic acid extracts  $\text{H}_2\text{SO}_4$  to give the



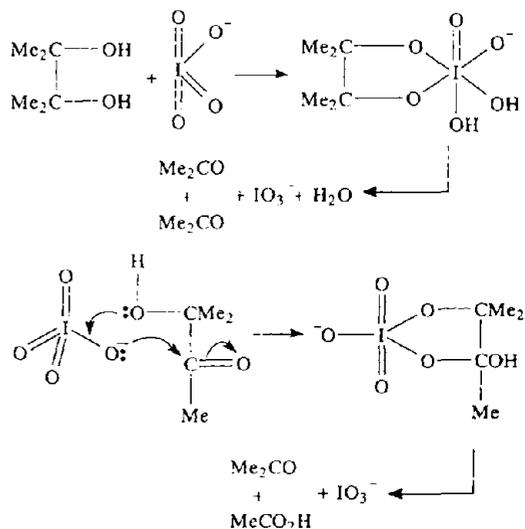
white, hygroscopic powder  $[\text{I}(\text{OH})_6]_2\text{SO}_4$ .<sup>[145]</sup> These compounds thus complete the series of octahedral hexahydroxo species  $[\text{Sn}(\text{OH})_6]^{2-}$ ,  $[\text{Sb}(\text{OH})_6]^-$ ,  $[\text{Te}(\text{OH})_6]$  and  $[\text{I}(\text{OH})_6]^+$ .

In aqueous solution increase in pH results in progressive deprotonation, dehydration and dimerization, the principal species being  $[(\text{HO})_4\text{IO}_2]^-$ ,  $[(\text{HO})_3\text{IO}_3]^{2-}$ ,  $[(\text{HO})_2\text{IO}_4]^{3-}$ ,  $[\text{IO}_4]^-$  and  $[(\text{HO})_2\text{I}_2\text{O}_8]^{4-}$ . The various equilibrium constants are:



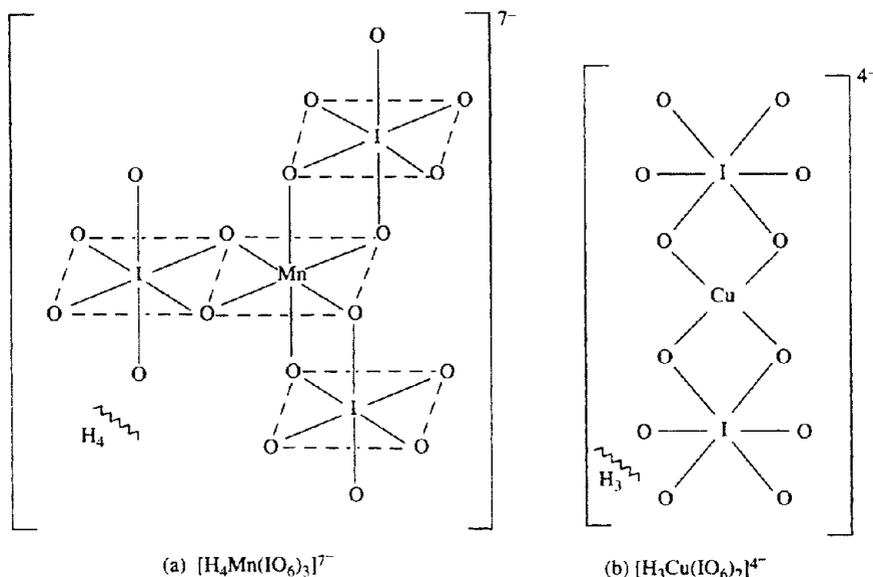
Periodates are both thermodynamically potent and kinetically facile oxidants. The oxidation potential is greatest in acid solution (p. 855) and can be progressively diminished by increasing the pH of the solution. In acid solution it is one of the

few reagents that can rapidly and quantitatively convert  $\text{Mn}^{\text{II}}$  to  $\text{Mn}^{\text{VII}}\text{O}_4^-$ . In organic chemistry it specifically cleaves 1,2-diols (glycols) and related compounds such as  $\alpha$ -diketones,  $\alpha$ -ketols,  $\alpha$ -aminoalcohols, and  $\alpha$ -diamines, e.g.:



<sup>[145]</sup> H. SIEBERT and U. WOERNER, *Z. anorg. allgem. Chem.* **398**, 193-7 (1973).

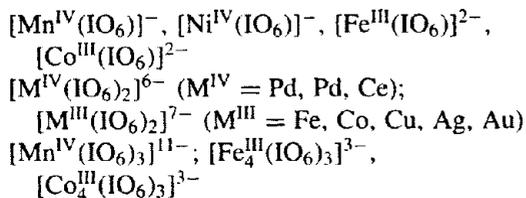
In rigid systems only *cis*-difunctional groups are oxidized, the specificity arising from the



**Figure 17.25** Structure of anions in  $\text{Na}_7[\text{H}_4\text{Mn}(\text{IO}_6)_3] \cdot 17\text{H}_2\text{O}$  and  $\text{Na}_3\text{K}[\text{H}_3\text{Cu}(\text{IO}_6)_2] \cdot 14\text{H}_2\text{O}$ .

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  $\text{IO}_6^{5-}$  unit acts as a bidentate chelate. Examples are:



The stabilization of  $\text{Ni}^{\text{IV}}$ ,  $\text{Cu}^{\text{III}}$  and  $\text{Ag}^{\text{III}}$  is notable and many of the complexes have very high formation constants, e.g.  $[\text{Cu}(\text{IO}_6)_2]^{7-} \sim 10^{10}$ ,  $[\text{Co}(\text{IO}_6)_2]^{7-} \sim 10^{18}$ . The high formal charge on the anion is frequently reduced by protonation of the  $\{\text{I}(\mu\text{-O})_2\text{O}_4\}$  moiety, as in orthoperiodic acid itself. For example  $\text{H}_{11}[\text{Mn}(\text{IO}_6)_3]$  is a heptabasic acid with  $\text{p}K_1$  and  $\text{p}K_2 < 0$ ,  $\text{p}K_3$  2.75,  $\text{p}K_4$  4.35,  $\text{p}K_5$  5.45,  $\text{p}K_6$  9.55, and  $\text{p}K_7$  10.45. The crystal structure of  $\text{Na}_7[\text{H}_4\text{Mn}(\text{IO}_6)_3] \cdot 17\text{H}_2\text{O}$  features a 6-coordinate paramagnetic  $\text{Mn}^{\text{IV}}$  anion (Fig. 17.25a) whereas

the diamagnetic compound  $\text{Na}_3\text{K}[\text{H}_3\text{Cu}(\text{IO}_6)_2] \cdot 14\text{H}_2\text{O}$  has square-planar  $\text{Cu}^{\text{III}}$  (Fig. 17.25b).

### 17.2.9 Halogen oxide fluorides and related compounds<sup>(146)</sup>

This section considers compounds in which X (Cl, Br or I) is bonded to both O and F, i.e.  $\text{F}_n\text{XO}_m$ . Oxofluorides  $-\text{OF}$  and peroxyfluorides  $-\text{OOF}$  have already been discussed (p. 638) and halogen derivatives of oxoacids, containing  $-\text{OX}$  bonds are treated in the following section (p. 883).

#### Chlorine oxide fluorides<sup>(147)</sup>

Of the 6 possible oxide fluorides of Cl, 5 have been characterized: they range in stability from the thermally unstable  $\text{FCl}^{\text{III}}\text{O}$  to the chemically rather inert perchloryl fluoride  $\text{FCl}^{\text{VII}}\text{O}_3$ . The others are  $\text{FCl}^{\text{V}}\text{O}_2$ ,  $\text{F}_3\text{Cl}^{\text{V}}\text{O}$  and  $\text{F}_3\text{Cl}^{\text{VII}}\text{O}_2$ .

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