10.4: Oxyacids of Chlorine

Table 10.4.1 lists the various oxyacids of chlorine. The relative strengths increase with the number of oxygen atoms since the more there are, the greater is the extent to which the negative charge on the resulting anion can be delocalized.

Table 10.4.1: Relative acidity of oxyacids of chlorine.

Oxyacid	Formula	pK_a
Hypochlorous	HOCl	7.5
Chlorous	$HClO_2$	1.9
Chloric	$HClO_3$	-2
Perchloric	$HClO_4$	-10

Hypochlorous acid

Hypochlorous acid (HOCl) can be made pure in the gas phase, (10.4.1), while strong acid solutions can be made from Cl_2O. In contrast, dilute aqueous solutions are obtained with a suspension of mercury oxide to remove the chloride, (10.4.2).

$$H_2O_{(g)} + Cl_2O_{(g)} \rightleftharpoons 2HOCl_{(g)} \tag{10.4.1}$$

$$2Cl_2 + 2HgO_{(s)} + H_2O \rightarrow 2HOCl + HgO \cdot HgCl_2 \downarrow \tag{10.4.2}$$

Solutions of the anion, OCl^-, are obtained by electrolysis of brine solution; allowing the products to mix at low temperature, (10.4.3).

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O \tag{10.4.3}$$

The anion (hypochlorite) is a good oxidant, (10.4.4) and (10.4.5), but can undergo disproportionation, (10.4.6); slowly at 25 °C, but fast above 80 °C.

$$ClO^- + NH_3 \rightarrow NH_2Cl + OH^- \tag{10.4.4}$$

$$ClO^- + 2I^- + 2H^+ \rightarrow I_2 + Cl^- + H_2O \tag{10.4.5}$$

$$3ClO^- \rightarrow 2Cl^- + ClO_3^- \tag{10.4.6}$$

Chlorous Acid

Chlorous acid (HOClO) is prepared by the reaction of ClO_2 with base, (10.4.7), followed by the precipitation of the ClO_2^- salt with barium chloride, (10.4.8). The barium salt is dried and then reacted with a calculated amount of H_2SO_4, (10.4.9).

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \tag{10.4.7}$$

$$2ClO_2^- + BaCl_2 \rightarrow 2Cl^- + Ba(ClO_2)_2 \downarrow \tag{10.4.8}$$

$$Ba(ClO_2)_2 + H_2SO_4 \rightarrow Ba(SO_4) + 2HClO_2 \tag{10.4.9}$$

The pure acid is unknown since it is too unstable, however, salts can be prepared directly, e.g., (10.4.10).

$$2ClO_2 + Na_2O_2 \rightarrow 2NaClO_2 + O_2 \tag{10.4.10}$$

The anion (ClO_2^-) is stable in alkaline solutions but in acid solutions decomposition occurs, (10.4.11).

$$5HClO_2 \rightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O \tag{10.4.11}$$

As with hypochlorite, the chlorite anion is a strong oxidant, (10.4.12).

$$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + 2H_2O + Cl^- \tag{10.4.12}$$

Chloric Acid

The chloric anion (ClO_3^-) is made from the reaction of chlorine gas with hot alkali (80 °C) or by the electrolysis of hot NaCl solution.

$$3Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- + 3H_2O \tag{10.4.13}$$

To obtain a solution of the acid, ClO_3^- is precipitated as the barium salt, (10.4.14), which is removed, dried, and suspended in water and treated with a calculated amount of H_2SO_4, (10.4.15). The free acid cannot be isolated and a maximum concentration of only 40% can be obtained in water.

$$2ClO_3^- + BaCl_2 \rightarrow 2Cl^- + Ba(ClO_3)_2 \downarrow \tag{10.4.14}$$

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow Ba(SO_4) + 2HClO_3 \tag{10.4.15}$$

The ClO_3^- anion is pyramidal both in solid salts and in solution, and many salts are known; however, those with organic cations are explosive. The anion is a strong oxidizing agent, (10.4.16) and (10.4.17), and it disproportionates slowly in solution, (10.4.18).

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + 3H_2O + Cl^- \tag{10.4.16}$$

$$ClO_3^- + 3NO_2^- \rightarrow 3No_3^- + Cl^- \tag{10.4.17}$$

$$4ClO_3^- \rightarrow 3ClO_4^- + Cl^- \tag{10.4.18}$$

Perchloric Acid

The perchlorate anion (ClO_4^-) is best made by electrolytic oxidation of chlorate in aqueous solution, (10.4.19). Fractional distillation can concentrate the solution to 72.5% which is a constant boiling mixture. This concentration is moderately safe to use, however, 100% perchloric acid may be obtained by dehydration with H_2SO_4.

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \tag{10.4.19}$$

WARNING

Perchloric acid is a very dangerous liquid that will explode if traces of metal ions are present. It is also a very strong oxidizing agent that will convert organic compounds to CO_2 and H_2O.

Perchloric acid is a very strong acid that is fully ionized in aqueous solution, such that the salt $[H_3O][ClO_4]$ can be isolated. Many other perchlorate salts are known, but those with organic cations are explosive. Perchlorate salts of metals are often used when studying complex formation in aqueous solution, because ClO_4^- is a very weak ligand (PF_6^- is better) and unlikely to form complexes itself. However, perchlorate does complex with +3 and +4 cations.