

## 10.4: Oxyacids of Chlorine

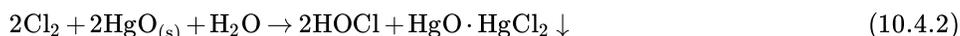
Table 10.4.1 lists the various oxyacids of chlorine. The relative strengths increase with the number of oxygen atoms since the more there are, the greater is the extent to which the negative charge on the resulting anion can be delocalized.

Table 10.4.1: Relative acidity of oxyacids of chlorine.

Oxyacid	Formula	pK <sub>a</sub>
Hypochlorous	HOCl	7.5
Chlorous	HClO <sub>2</sub>	1.9
Chloric	HClO <sub>3</sub>	-2
Perchloric	HClO <sub>4</sub>	-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<sub>2</sub>O. In contrast, dilute aqueous solutions are obtained with a suspension of mercury oxide to remove the chloride, (10.4.2).



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

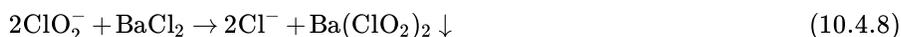


The anion (hypochlorite) is a good oxidant, (10.4.4) and (10.4.5), but can undergo disproportionation, (10.4.6); slowly at 25 °C, but fast above 80 °C.



### Chlorous Acid

Chlorous acid (HOClO) is prepared by the reaction of ClO<sub>2</sub> with base, (10.4.7), followed by the precipitation of the ClO<sub>2</sub><sup>-</sup> salt with barium chloride, (10.4.8). The barium salt is dried and then reacted with a calculated amount of H<sub>2</sub>SO<sub>4</sub>, (10.4.9).



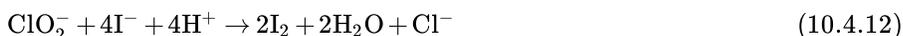
The pure acid is unknown since it is too unstable, however, salts can be prepared directly, e.g., (10.4.10).



The anion (ClO<sub>2</sub><sup>-</sup>) is stable in alkaline solutions but in acid solutions decomposition occurs, (10.4.11).



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



## Chloric Acid

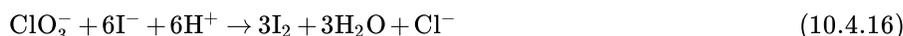
The chloric anion ( $\text{ClO}_3^-$ ) is made from the reaction of chlorine gas with hot alkali (80 °C) or by the electrolysis of hot NaCl solution.



To obtain a solution of the acid,  $\text{ClO}_3^-$  is precipitated as the barium salt, (10.4.14), which is removed, dried, and suspended in water and treated with a calculated amount of  $\text{H}_2\text{SO}_4$ , (10.4.15). The free acid cannot be isolated and a maximum concentration of only 40% can be obtained in water.



The  $\text{ClO}_3^-$  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).



## Perchloric Acid

The perchlorate anion ( $\text{ClO}_4^-$ ) 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  $\text{H}_2\text{SO}_4$ .



### 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Perchloric acid is a very strong acid that is fully ionized in aqueous solution, such that the salt  $[\text{H}_3\text{O}][\text{ClO}_4]$  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  $\text{ClO}_4^-$  is a very weak ligand ( $\text{PF}_6^-$  is better) and unlikely to form complexes itself. However, perchlorate does complex with +3 and +4 cations.

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