

CHAPTER 2

Biological Significance and Uses of Chlorine Oxyanion Chemistry

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Abstract: Chlorine oxyanions (ClO_n^- , where n is ranging from 1-4) with oxidation states ranging from +1 to +7 have been utilized as oxidants for many years. Rocket fuel propellants and bleaching agents are among their uses. The chlorine oxidation state of the pertinent chlorine oxyanion, chlorite (ClO_2^-), is +3. This oxyanion is used in the pulp bleaching business to create ClO_2 , however chlorate is preferred because it is less expensive and produces fewer corrosive conditions and byproducts. There is industrial interest in a catalytic method of converting chlorite into chlorine dioxide.

Keywords: Chlorine oxyanions, chlorine dioxide, chlorite dismutase, water purification

Introduction

The oxyanions of chlorine (ClO_n , n = 1 to 4), exhibiting oxidation states from +1 to +7, have many applications, including rocket fuel and bleaching agents. The sources of water become polluted by

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this detrimental contaminant because to its extensive usage and significant solubility in water.¹ In recent decades, the elimination of these species from aquatic and environmental sources has attracted significant attention.²⁻⁵ In an acidic medium, the oxyanions of chlorine act as potent oxidizing agents. Only two stable chlorine anhydrides exist among all contemporary chlorine oxyanions. The two anhydrides namely are oxygen dichloride (Cl_2O) and the other one chlorine dioxide (ClO_2).

Furthermore, another two mixed anhydrides having dichlorine hexoxide (Cl_2O_6) and other interesting species dichlorine heptoxide (Cl_2O_7). Although another anhydride can also be produced, these anhydrides are highly unstable.⁶ Their uses have evolved over time due to the introduction of new markets and, more recently, regulatory developments prompted by critical environmental issues and the contamination of drinking water. For strong existence of human in the earth centre it is still believed that these chlorine oxyanions are decisive. This page addresses the significance of the four chlorine oxyanions, including their natural occurrence, industrial synthesis, toxicity, and bioremediation potential.⁷⁻¹³

Perchlorate (ClO_4^-) having chlorine as central metal ion is +7 oxidation state, widely used in rocket fuel, fireworks, and missile.^{6, 8} Handling of the perchlorate compound or having perchlorate anions should have extreme care. The remediation or removal of perchlorate with microbes as well chemical treatment from water sources has been used efficiently.⁸⁻⁹ Due to the sensitivity and thermal uncertainty, meticulous precautions are necessary when handling this molecule and others containing anions as perchlorate. Perchloric acid, most formidable Brønsted-Lowry acids, having pKa of value of -10.⁸ In water as solvent, it engages themselves with various reagent like metals, metal oxides, hydroxides, and salts of volatile acids, yielding the corresponding anion. It is the minimum potent oxidizing agent ($E^0 = 1.42 \text{ V vs. SHE for } \text{ClO}_4^-/\text{Cl}_2$) among the chlorine oxyanions and exhibits a rather slow reaction rate.⁵

Water sources in the environment can become seriously contaminated due to its extensive usage, production, and very sluggish response.⁸ One Usually, ion-exchange resins are used to safely remove perchlorate, subsequently filter and finally an oil-water separation.⁹ Nevertheless, certainly these methods are protracted and comparatively affluent. As early as the 1880s, naturally occurring perchlorate was found in the Atacama Desert's terrestrial nitrate deposits in Chile.¹⁰ The exact reason is still a mystery, but several hypotheses have been advanced to explain it, such as heat or UV chlorine oxidation, lightning chloride activation, ozone or photochemical species oxidation, and others.¹¹⁻¹³ Recent developments in ion-exchange chromatography have increased the availability of natural perchlorate.¹⁴⁻¹⁶ This method separates polar molecules and ions according to their charges. Perchlorate is produced in an industrial setting by electrolyzing chlorate (Eq. 1.1).

In these chlorine oxyanions, chlorate (ClO_3) is the next oxidation state of chlorine (+5). The primary usage of this oxyanion is as a precursor to chlorine oxyanion, which is then converted into chlorine dioxide (ClO_2) for use in wood pulp bleaching.¹⁷ In chemical oxygen generators used by commercial airlines, chlorate is used as a dioxygen source; it also defoliates and desiccants cotton and soybean, in that order.¹⁸⁻¹⁹ Additionally, it is used as an herbicide. Chloric acid is a potent acid with a

pKa that is actually a stronger oxidising agent than perchlorate of -1 ($E^0 = 1.47$ V vs. SHE for $\text{ClO}_3^-/\text{Cl}_2$).⁵ It will dissolve easily into several reagent like oxygen, chlorine, chlorine dioxide, and perchloric acid with a raise the temperature of a chloric acid solution to more than 95°C .⁵ There is naturally occurring chlorate on Earth, with deserts having the highest quantities. Rainfall samples have shown both chlorate and perchlorate at comparable concentrations, which could indicate that they share a common source in the chlorine biogeochemical cycle.²⁰ Twenty-four As shown in Eq. 1.2, the electrolysis of chlorine gas (Cl_2) is the main method for industrial chlorate production.

Chlorite (ClO_2^-) is the name given to the next and most intriguing oxidation state of chlorine (+3) seen in these chlorine oxyanions. With many of its uses, chlorite obliges as a bleaching agent and is exploited in the generation of ClO_2 within the pulp bleaching segment.⁵ Nevertheless, chlorate is favored owing to financial factors, including its lower corrosiveness and the minimal generation of byproducts. Toothpastes, therapeutic rinses, oral sprays, mouthwashes, and ophthalmic solution preservatives are just a few of chlorite's many commercial uses, especially when mixed with zinc chloride.

Chlorous acid is pigeon-holed as a feeble acid, holding a pKa value of 1.96, and is recognized for its superior efficacy as an oxidizing agent in comparison to chlorite ($E^0 = 1.64$ V vs. SHE for $\text{HClO}_2/\text{Cl}_2$).⁵ Chlorite fails to be acknowledged as a naturally occurring substance owing to its comparative instability when juxtaposed with chlorate and perchlorate. According to Eq. 1.3, the standard procedure for synthesising chlorite comprises disproportioning chlorine dioxide in a basic environment to produce chlorite and chlorate.

Hypochlorite (ClO^-) is the name given to the chlorine oxyanions that have the least amount of chlorine in its oxidation state (+1). Both as a decontaminator and, more often, a bleaching agent, this chlorine oxyanion sees widespread use.⁵ Hypochlorite, owing to its heightened reactivity, is available in commercial solutions with concentrations ranging from 1% to 25%, as opposed to being provided in solid form like other name's sake of chlorine oxyanions.

The pK_a value of hypochlorous acid is 7.53, demonstrating that it is a weak acid. The most potent oxidizing agent among the chlorine oxyanions ($E^0 = 1.63$ V SHE for HClO/Cl_2).⁵ Hypochlorous acid is biologically produced in active neutrophils through the myeloperoxidase-mediated peroxidation of chloride ions, aiding in bacterial eradication. Twenty-five to twenty-seven Hypochlorite is infrequently utilized for drinking water disinfection due to the formation of minor quantities of more harmful chlorinated byproducts. The same grounds as chlorite explain why hypochlorite isn't considered a naturally occurring chemical. Eq. 1.4 shows that hypochlorite and chloride are formed when chlorine gas is added to a basic solution, which is the process used in industrial manufacturing.

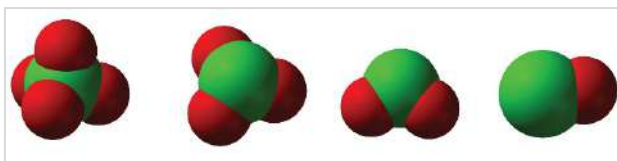
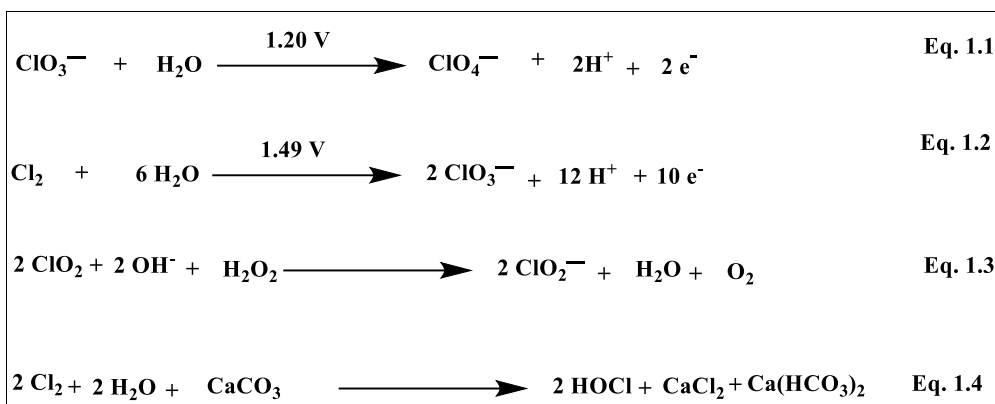
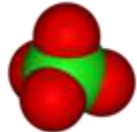
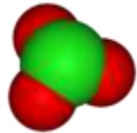
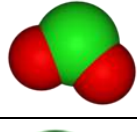
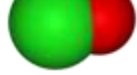


Figure 1: The different oxyanaions of chlorine²⁴

**Table 1:** Properties and uses of various oxyanions of chlorine^{24, 5}

Name	Formula	Chlorine oxidation state	Uses	Picture
The perchlorate ion	ClO_4^-	+7	Rocket fuel, fireworks, and missile	
The chlorate ion	ClO_3^-	+5	Bleaching agent	
The chlorite ion	ClO_2^-	+3	Bleaching agent	
The hypochlorite ion	ClO^-	+1	Disinfectant and bleaching agent	

Environmental Concerns: Accumulation and Toxicity

The extensive applications and high solubility of harmful anthropogenic pollutants have led to considerable contamination of water sources. Chemical and physical technologies are traditional methods. Water treatment fails to adequately eliminate hazardous contaminants, leading to health and biological problems associated with each specific chlorine oxyanion. Chlorine oxyanions exhibit toxicity to humans, although their effects differ. Perchlorate inhibits thyroid hormone production essential for proper development and growth by competing with the sodium-iodine symporter.²⁵ The Environmental Protection Agency (EPA) reports that 11 million Americans live in provinces where perchlorate levels exceed the permissible perimeter in public drinking water. The remediation of perchlorate has progressed via the utilisation of microorganisms and chemical catalysts.²⁶ Hutchinson et al. conducted a

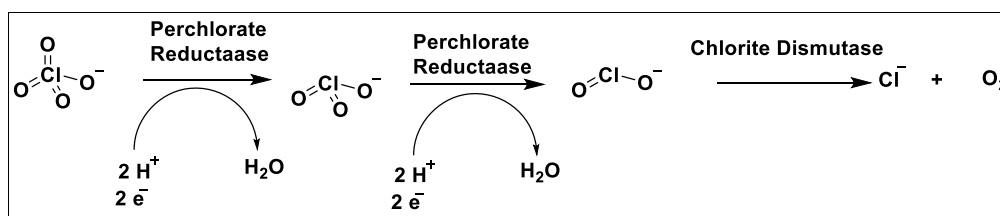
study on the use of enzymes within a cell-free system for perchlorate remediation.²⁷ The removal of perchlorate is hindered by its sluggish reactivity with most reducing agents. In below examines the effects of oxyanions on human health and the environment, reviews techniques for their detection in aquatic systems, and evaluates methods for their removal from aqueous environments.²⁸

Table 2: Presence of halogen oxyanions in aqueous environments.²⁸

Name	Found in	Analytical method for Removal
ClO_4^-	River water, Drinking water, Groundwater, Mineral water, Swimming pool etc.	Ion chromatography, Ion chromatography-electrospray ionization-mass spectrometry (IC-ESI-MS)
ClO_3^-	Drinking water, NaClO solution,	Spectrophotometry
ClO_2^-	Drinking water	UV/vis spectrophotometry

Biological Importance

It is found that Perchlorate-respiring bacteria famously known as “PRB” exploit these oxyanions of chlorine as metabolic oxidants for inhalation, giving a captivating outlook for bioprocesses.²⁹⁻³⁰ Although the process of perchlorate remediation reveals in three discrete stages, eased by the feat of two distinct enzymes. The presence of iron-sulfur clusters, molybdenum, and selenium, in perchlorate reductase—an oxygen subtle enzyme situated in the periplasm—enables electron transport. Enzyme activity suggests a chlorate intermediate of perchlorate to chlorite by means of the four-electron reduction. One possible substitute enzyme is chlorite dismutase, or Cld. Its main function is to produce chloride (Cl^-) and dioxygen (O_2) from chlorite.³¹⁻³⁴



Scheme 1. Production of oxygen and chloride from perchlorate by enzyme.



Figure 2: Crystal structure of the perchlorate reductase(PDB No. 5E7O)

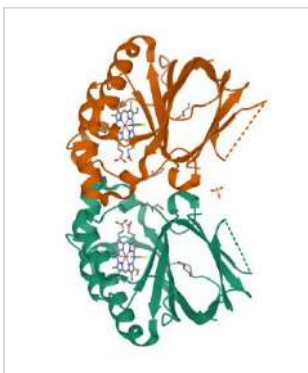


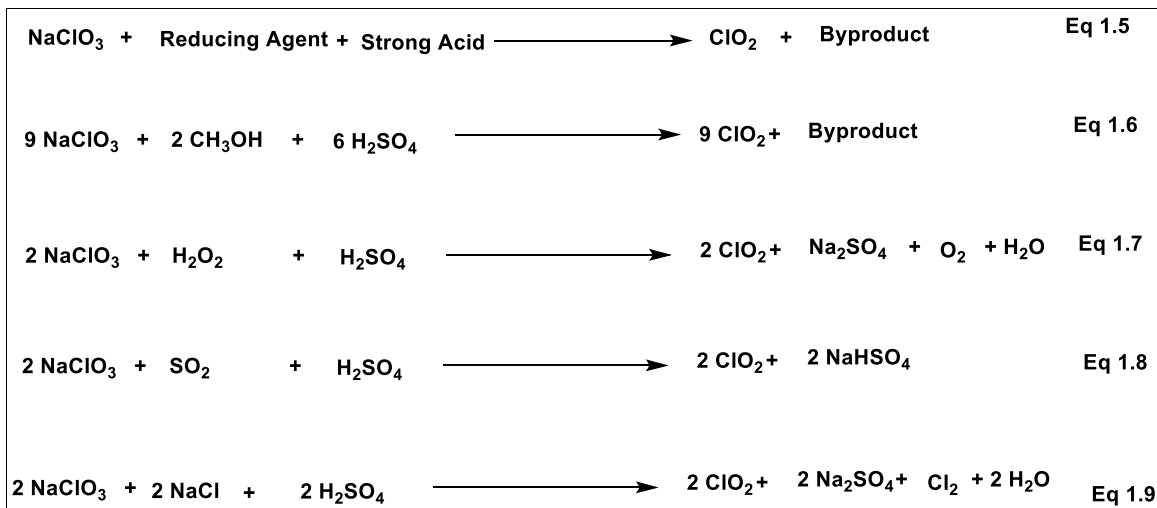
Figure 3: Crystal structure of dimeric chlorite dismutase from *Cyanothoece* (PDB No. 5K90)

The Manufacturing and Application of Chlorine Dioxide in Industry

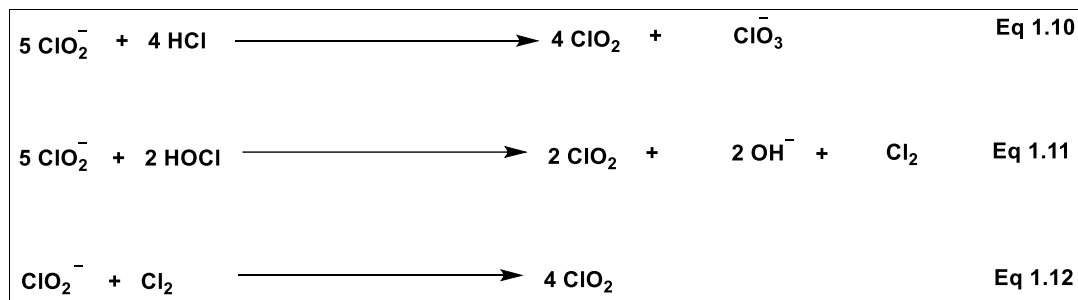
The paramagnetic nature of the gaseous chlorine dioxide, which has an odd number of electrons, gives it a yellowish-green hue. It stays in gaseous form in solution but has a high-water solubility (around 8 g/mL at 20 °C). As an oxidising agent, chlorine dioxide finds its primary use in pulp bleaching and water disinfection or treatment in the commercial sector. Careful handling methods are required due to the severe toxicity of chlorine dioxide. The 0.8 mg/L maximum chlorine dioxide concentration in drinking water was set by the EPA, whereas the 0.1 ppm air exposure limit was set by OSHA for 8 hours. A total of 72 Because of its superior antibacterial effectiveness and decreased production of hazardous by-products, chlorine dioxide is preferred to chlorine gas (Cl_2) for water treatment. The fact that ClO_2 becomes very unstable at high pressure makes it very difficult to transport as a gas, which is a major drawback. As a result, any real-world use requires the on-site manufacture of ClO_2 .

There are many industrial chlorine dioxide production processes. In all cases, ClO_2 comes from chlorine oxyanions (ClO_n^-). Method. Most procedures use powerful oxidants and corrosive conditions, posing health and environmental risks. 72 Eq. 1.5 shows the main ClO_2 generation reaction using chlorate, a reducing agent, and a strong acid. Eq. 1.6 states that concentrated sulphuric acid and methanol are the industry standards for strong acids and reducing agents. This process produces several compounds namely water, carbon dioxide, formic acid and sodium sesquisulfate. Bleaching is unaffected by carbon dioxide and formic acid generation. Sulphuric acid's strength helps produce sodium sesquisulfate. To convert sodium sesquisulfate into sodium sulfate and sulfuric acid, separate this solid and transfer it to a mixing/metathesis tank. The sulphuric acid that has been recovered is then recycled and used as a low-cost reagent for the chlorine dioxide reactor. Kraft pulping uses sodium sulfate to turn wood into pulp. Because of their affordability and dependability, these reactants are used by most chlorine dioxide manufacturers. With 10–20 stages and competing and parallel routes, the reaction is complicated. It is crucial to precisely regulate the concentrations and purity of reactants in order to optimise yields. Methods involving chlorates are illustrated in Scheme 1.4, which is based on the fundamental reaction scheme (Eq. 1.4). Despite the fact that chlorite production is not cost-effective, Scheme 1.5 shows a multitude of small-scale strategies for producing chlorine dioxide. The primary

processes include acid activation (Eq. 1.10) and chlorine activation (Eq. 1.11-1.12). The one-electron electrochemical oxidation of chlorite provides an alternative pathway to ClO_2 ; however, it necessitates a significant energy input. Consequently, a catalytic process warrants attention from an exploration from an environmental perspective and its advantages.



Scheme 2. Manufacture of chlorine dioxide from sodium chlorate is illustrated as in industrial scale.



Scheme 3. Manufacture of chlorine dioxide from sodium chlorite is illustrated.

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