# Oxychlorination of organic compounds

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Chloroorganic compounds are widespread in environment and are used in many areas. Chlorinated paraffins are produced, among others, by the marine alga [1, 2]. Compounds such as PCBs and DDT have been detected even in fish from lakes located in the Swiss Alps at an altitude of 2,062 to 2,637 m above sea level [3].
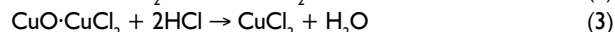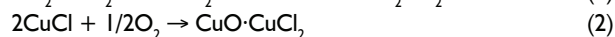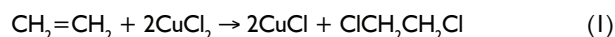
Oxychlorination involves the precursor of reactive oxygen species and chloride anion [4]. Applying this method is associated with the use of hydrogen chloride which is formed as a byproduct of many technologies [4]. The importance of this issue can be proved by the fact that in the USA hydrogen chloride preparation from elements is less than 10% of the total production of this commodity [5].

Oxychlorination of organic compounds is also a process that occurs in the environment. For example, chlorinated dioxins and furans can be formed as a result of transformations that occur in peatlands [6].

The catalysts for this process are enzymes called haloperoxidases [6]. They can be found, among others in fungi and bacteria [7]. Presence of haloperoxidases in soil, causes the introduction of chlorine isotope with mass number of 36 to humic substances [7]. Depending on the kind of reagents and haloperoxydase, $Cl^+$, $Cl^-$, $ClO$ and $Cl^\bullet$ could act as a chlorination agent [2, 8]. The enzyme myeloperoxidase is responsible for fighting infection by producing hypochlorous acid (I) [7] This compound is a thousand times more active in the fight against certain strains of bacteria than $H_2O_2$ [7]. Marine organisms use high concentrations of $Cl^-$ ions in the salt waters in order to synthesize organochlorine compounds needed for defense against pathogens [9]. Many of these substances are used as antiviral and antibacterial drugs [9]. In recent years an intensive studies on telluroorganic compounds have been carried out in order to find catalysts with a similar activity to haloperoxydases [10]. An interesting example of catalysts used for aromatic compounds oxychlorination are copper, iron and cobalt phthalocyanines supported on zeolites [11]. Studies showed that phthalocyanines containing substituents such as -Cl and -NO$_2$ are more active than unsubstituted [11].

In oxychlorination process phase-transfer catalysis is also applied [12]. For example, benzene can be oxychlorinated very efficiently by using $H_2O_2$/HCl system in the presence of quaternary ammonium salt [12].

Oxychlorination is probably most associated with the production of vinyl chloride. In Poland „ANWIL" S.A in Włocławek uses this technology. This process consists of the following chemical reactions (1÷3) [13]:

$$CH_2=CH_2 + 2CuCl_2 \rightarrow 2CuCl + ClCH_2CH_2Cl \quad (1)$$
$$2CuCl + 1/2O_2 \rightarrow CuO\cdot CuCl_2 \quad (2)$$
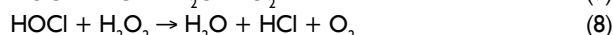$$CuO\cdot CuCl_2 + 2HCl \rightarrow CuCl_2 + H_2O \quad (3)$$

Copper chloride (II) supported on a carrier is a catalyst of this process [13]. Oxychlorination of ethylene is carried out in a temperature range of 170°C to 400°C [13]. Copper chloride (II) is also used in oxychlorination processes leading to phosgene [14], allyl chloride [15] and chlorobenzene [16].

Hydrogen peroxide is one of the reactive oxygen sources. There are several hypothetical mechanisms and kinetic models that have been proposed to describe the transformations occurring in the HCl/$H_2O_2$ system [4]. Skudaev and co-workers studied the oxidation of hydrochloric acid with the use of hydrogen peroxide [17]. The concentration of hydrogen peroxide was 30% [17]. Reaction was carried out in a temperature range of 25°C to 75 °C [17]. Based on the amount of evolved chlorine and oxygen the fallowing kinetic equation (4) has been proposed [17]:

$$v=4.8\cdot 10^{13} exp\left(-\frac{E}{RT}\right) c_8^{1.1} c_2^{2.3} \quad (4)$$

In equation (4) $v$ is the rate of evolution of oxygen from the reaction mixture, E is the activation energy (100 kJ/mol$^1$), $c_2$ is the concentration of hydrogen peroxide [17]. Threshold concentration of HCl $c_e$ is 5.2 mol/dm$^3$ [17]. Exceeding this value causes the evolution of chlorine from the reaction mixture [17]. According to the authors, the form of kinetic equation and the existence of the threshold concentration of HCl confirm the correctness of the following mechanism (5÷9) [17].

$$H_2O_2 + HCl \rightarrow H_2O_2\cdot HCl \quad (5)$$
$$H_2O_2\cdot HCl \rightarrow H_2O + HOCl \quad (6)$$
$$HOCl + HCl \rightarrow H_2O + Cl_2 \quad (7)$$
$$HOCl + H_2O_2 \rightarrow H_2O + HCl + O_2 \quad (8)$$
$$H_2O_2 + Cl_2 \rightarrow 2HCl + O_2 \quad (9)$$

An interesting issue is the transformations of aromatic amines in the presence of chloride ion and hydrogen peroxide. Aniline is likely to be oxychlorinated according to scheme (10) [4]:
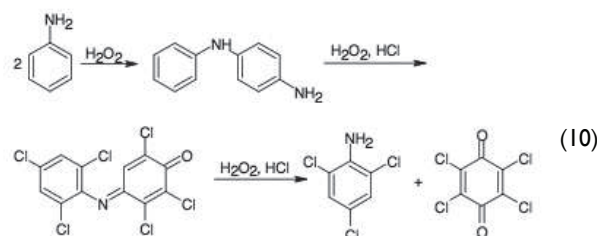


If the ratio of [$H^+$]:[$Cl^-$]:[$H_2O_2$] ranges from (1:1:1) to (1:1:2), in the final product equal amounts of 2,4,6-trichloroaniline and 2,3,4,6-tetrachloro-2,3,5-trichlorobenzoquinone and small amounts of 2-chloroaniline, 4-chloroaniline and various products of oxidation can be found in reaction mixture [4]. On the other hand, if the excess of hydrochloric acid in relation to the hydrogen peroxide is at least seven times, 2,4,6-trichloroaniline is mainly produced [4].

Aromatic compounds containing electron donating substituents such as -OH and -NH$_2$ react rapidly with the oxychlorinating mixtures [18]. Oxychlorination of alkyl derivatives of aniline leads to quinones [18]. This can be prevented by using acylated aromatic amines in the process [18]. There were carried out studies on the oxychlorination of acetanilides using a variety of acids and metal chlorides [4]. The highest yield and the degree of conversion were obtained using lithium, sodium, potassium and aluminum chloride [4]. *In case of using* cobalt (II), manganese (II), nickel (II), copper (II) and iron (III) chloride products of oxydation have been found, the quantity of which increases with the growth of temperature [4]. The highest yield and the degree of conversion were obtained using HClO$_4$ and H$_2$SO$_4$ [4]. Substituent effect on the chlorination reaction of acetanilides with the use of NaCl, H$_2$O$_2$ and HNO$_3$ was studied (29) [4]. Yield of chlorinated compounds and the degree of

conversion depends on the type and position of substituents [4]. Acetanilides with electron acceptor groups like -NO$_2$ are chlorinated with higher yield than acetanilides with electron donating substituents such as -CH$_3$, -OCH$_3$ [4].

Depending on the type of chloride, different yields of *p*-nitroaniline oxychlorination products were obtained [4]. When MCl$_x$/HNO$_3$/H$_2$O$_2$ oxychlorinating system was used (where M$^{x+}$ = Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Fe$^{3+}$) yields varied in the range [4]: LiCl > NaCl > AlCl$_3$ > KCl > CaCl$_2$ ≥ MnCl$_2$ > CoCl$_2$ > NiCl$_2$ > CuCl$_2$ ≥ FeCl$_3$ > ZnCl$_2$. When the oxychlorination mixture consists of metal chloride, sulfuric acid and hydrogen peroxide the situation is different (LiCl > CoCl$_2$ > AlCl$_3$ ≥ NaCl > MnCl$_2$ > CaCl$_2$ > CuCl$_2$ ≥ KCl > NiCl$_2$ ≥ FeCl$_3$ > ZnCl$_2$) [4]. It was fund that the growth of hydronium ion concentration in the reaction with *p*-nitroaniline and HCl/NaCl/(NH$_4$)$_2$S$_2$O$_8$ system causes the increase of yield [19]. As it is well known, the ammonium nitrogen atom direct attacking electrophiles to the *meta* position [19] However, product corresponding to the mechanism of electrophilic substitution was not found [19].

Studies on the oxychlorination of sulphanilic acid showed that besides of chlorinated derivatives of sulphanilic acid, 2,4,6-trichloroaniline 2,4-dichloroaniline and 4-chloroaniline were also formed [4]. This process is best carried out with a large excess of oxychlorinating mixture in a temperature range of 15°C to 50°C [4].

There have been attempts to determine the oxychlorination mechanisms by means of computational methods [20]. An interesting example are studies of transformations occurring in systems containing oxychlorinating systems and *tert*-butyl ethers. [20]. The following reaction paths ware proposed (Fig. 1) [20]:
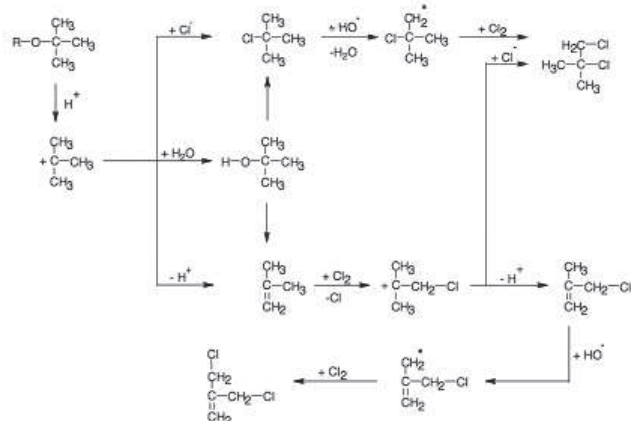


**Fig. 1. Reactions path of *tert*-butyl ethers**

As calculations showed both radical and ionic pathways are thermodynamically possible [20]. However, radical mechanism is more likely [20].

Studies on the oxychlorination process involved different groups of compounds. For sure the biggest benefits of using mentioned in this paper methods are the development for the waste hydrogen chloride and elimination of toxic chlorine. Not exactly clear mechanisms of some of these processes is an interesting challenge to take on new research.

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*Translation into English by the Author*

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