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Thionyl Chloride (CAS No 7719-09-7)

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Thionyl Chloride ($SOCl_2$, **1**, Figure 1) is a colorless to pale yellow liquid, molecular weight 118,97, boiling point at 76 °C, miscible in carbon tetrachloride, benzene and chloroform, density 1.631 g.cm^{-3} and smell similar to sulfur dioxide (SO_2).[1]

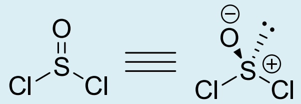

Figure 1. Chemical structure of Thionyl Chloride **(1)**.

The chemical structure of thionyl chloride presents an electrophilic center (sulfur atom at sulfoxide) and two leaving groups (chlorine atoms in sulfoxide). These structural features are responsible for the chemical versatility of thionyl chloride, which is applied in several synthetic methodologies to obtain several intermediaries and chemical products in agrochemistry, fine chemistry, and pharmaceuticals. [2,3]

The most common uses of **1** in chemistry are: (a) the production of acyl chloride and sulfuryl chloride, [2,3] using the corresponding carboxylic acids and sulphonic acids as a raw material, and (b) the production of alkyl chlorides, using alcohols or thiols (marcaptans). [1,4,5] Yet, **1** is also applied in synthesis of sulfur heterocycles, imidoyl chlorides, *gem*-dichlorides from α-β unsaturated or aromatic aldehydes, in amide dehydration to nitriles and in the synthesis of diaryl sulfones.[2,3,5]

Thionyl Chloride **(1)** is also used in thionyl chloride-lithium (Li-$SOCl_2$) batteries. In these batteries, the metallic lithium is the anode and the cathode is porous carbon filled with **1**. The Li-$SOCl_2$ batteries presents as advantages long storage periods and a service life longer than 10 years. [6]

China and India are the main producers of $SOCl_2$, with an annual production estimated at 45,000 tons.[7,8]

The acquisition, importation and distribution of **1** in Brazil is regulated by the Federal Police (*Polícia Federal*). [9] This legal aspect hinders the access by researchers, research laboratories, and chemical industries to this important chemical reagent.

The industrial production of $SOCl_2$ is expensive and requires specific facilities to contain and handle the reactants, products and impurities in an eco-friendly manner, as those are usually toxic gases.[10] Several methodologies to produce $SOCl_2$ at an industrial scale have been described in patents, and most of them use SO_2 for the production of $SOCl_2$.[,11-14]

One of the oldest methods of thionyl chloride preparation consists in reacting phosphorus pentachloride (PCl_5) and SO_2 (Scheme 1). This method is extremely expensive, because it uses PCl_5 as reactant, presents low yields, and a difficult separation through the distillation of products.[11]

Hallowell and Vaala described a process that uses SO_2 and carbon tetrachloride (CCl_4) or chloroform ($CHCl_3$), and a Friedel-Crafts catalyst (ex. $AlCl_3$, $AlBr_3$, $FeCl_3$), in extreme temperatures (140 to 400 °C) and pressure (15 to 200 atm) conditions to produce **1** (Scheme2).[12] Nevertheless, this process ignores that when heated above 140 °C, **1** decomposes to chlorine (Cl_2) , SO_2, and disulfur dichloride(S_2Cl_2) (Scheme 3) and that the presence of iron turns **1** darker (pale yellow to reddish).[14]

The production of $SOCl_2$, using sulfur chloride (SCl_2), Cl_2, and sulfuric acid (H_2SO_4), presents as drawbacks the formation of SO_2 and hydrochloric acid (HCl) (Scheme 4), that were not reused in the process due to the lack of adequate facilities, encumbering and preventing industrial production through this method.[10]

More recent processes propose the use of easily available and cheaper materials and in many cases, they allow for the reuse of industrial waste of other processes in the production of **1** at temperatures below 100°C, to avoid the formation of impurities due to the thermal decomposition of $SOCl_2$.[13,14]

The production of $SOCl_2$ has also been suggested through reacting SO_2, Cl_2 and S_2Cl_2 or SCl_2, using activated carbon as catalyst (Scheme 5).[10]

Using SO_2, Cl_2 and different carbon sources (e.g., wood, bone, coal, and sugar), containing activated metals after treatment with hydrochloric acid as a catalyst, **1** can be produced in good yields (Scheme 6).[13]

Thionyl Chloride **(1)** can also be simultaneously produced with phosphoryl chloride ($POCl_3$) by reacting phosphorus trichloride (PCl_3) and sulfuryl chloride (SO_2Cl_2). John E. Hill proposed an integrated process that reuses waste from other manufacturing processes and monitors the steps of the industrial production of **1** using colorimeters to optimize production yield and facilitate the separation of the final products, without unused reagents, in a quantitative manner.[14]

In Hill's process, in step 1,

$$SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$$

Scheme 1. Synthesis of **1** using sulfur dioxide and phosphorous pentachloride

$$\textbf{(A)}\ SO_2 + CCl_4 \longrightarrow SOCl_2 + CO_2$$
$$\textbf{(B)}\ SO_2 + CHCl_3 \longrightarrow SOCl_2 + CO + HCl$$

Scheme 2. Synthesis of **1** using sulfur dioxide and carbon tetrachloride **(A)** or chloroform **(B)**.

$$2\ SOCl_2 \xrightarrow{\triangle} 3/_2\ Cl_2 + SO_2 + 1/_2\ S_2Cl_2$$

Scheme 3. Thermal decomposition of **1.**

$$2\ H_2SO_4 + 3\ SCl_2 + Cl_2 \rightleftharpoons 2\ SOCl_2 + 3\ SO_2 + 4\ HCl$$

Scheme 4. Synthesis of **1** using sulfuric acid, sulfur chloride and chlorine.

$$\textbf{(A)}\ S_2Cl_2 + 2\ SO_2 + 3\ Cl_2 \rightleftharpoons 4\ SOCl_2$$
$$\textbf{(B)}\ SCl_2 + 2\ SO_2 + 2\ Cl_2 \rightleftharpoons 2\ SOCl_2$$

Scheme 5. Synthesis of **1** using sulfur dioxide, chlorine and disulfur dichloride (A) or sulfur chloride **(B)**.

$$SO_2 + Cl_2 \xrightarrow{\text{catalyst}} SOCl_2 + 1/_2\ O_2$$

Scheme 6. Synthesis of **1** using chlorine and sulfur dioxide.

SO_2Cl_2 is produced by the reaction between SO_2 and Cl_2 catalyzed by silica gel or activated carbon. In step 2, there is the reaction between the SO_2Cl_2 produced in step 1 and PCl_3 in non-stoichiometric ratio, inside a reactor continuously filled with Cl_2 and SO_2, to form a mixture A containing **1**, $POCl_3$ and PCl_3 that in an integrated and continuous manner is shifted to step 3, where the mixture receives the addition of A, SO_2 and Cl_2 for the complete consumption of PCl_3, and to obtain a mixture containing only **1** and $POCl_3$, which are subsequently separated through fractional distillation (Figure 2).

In the industrial production of **1,** impurities such as SO_2Cl_2, S_2Cl_2 and SCl_2, can be observed and are responsible for changes in the reagent color. For purification of $SOCl_2$, fractional distillation with triphenylphosphine is recommended. [15]

Thionyl chloride **(1)** reacts violently with water, releasing vapors of HCl and SO_2.[1] Thus, the chemical reactivity associated to chemical structure of **1** should be considered on storage of this reagent, avoiding stocking **1** with nucleophilic nature compounds such as amines, ammonia and other Lewis bases, being kept in cool, dry, well ventilated and sealed containers that protect the flask from physical damage and moisture. [15] Thionyl Chloride **(1)** must be carefully handled, because it is irritating and can cause severe burns to eyes, membranes and skin that have been exposed to this chemical.[1,16,17]

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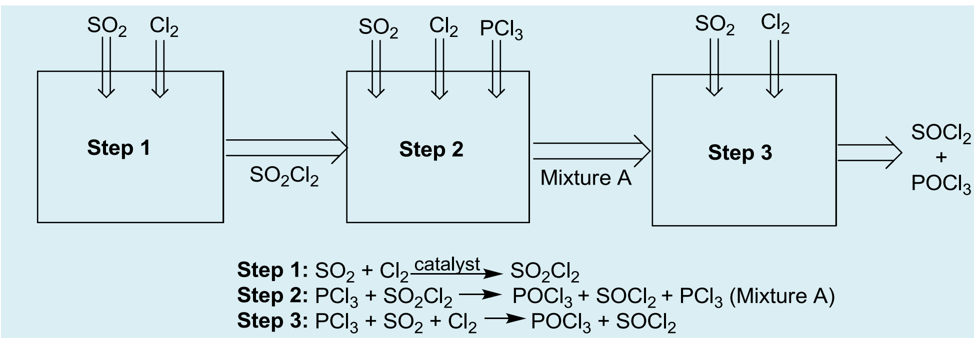

Figure 2. Schematic representation of Hill's process for obtaining **1**.

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Thionyl Chloride (CAS No 7719-09-7)

Abstract: Thionyl chloride is a colorless liquid (sometimes pale yellow due to impurities), molecular weight 118.97, boiling point 76 °C, soluble in carbon tetrachloride, benzene and chloroform, density 1.631 g.cm^{-3} and smell resembling that of sulfur dioxide (SO_2). This reagent is highly versatile and is used in several synthetic methodologies to obtain several intermediaries and chemicals of interest in agrochemistry, fine chemistry and pharmacy. The industrial production of thionyl chloride is expensive and specific facilities are required to contain and handle the reagents, products and impurities in an eco-friendly manner. Several methodologies of production of this reagent are described and most of them use sulfur oxides. Thionyl chloride must be carefully handled, because this reagent can cause irritation and severe burns to eyes, membranes and skin.

Keywords: Thionyl chloride; industrial scale production; sulfur oxides.

Resumo: Cloreto de tionila é um líquido incolor (ou amarelo pálido, devido a impurezas), peso molecular 118,97, ponto de ebulição 76 °C, solúvel em tetracloreto de carbono, benzeno e clorofórmio, com densidade 1,631 g.cm^{-3} e odor semelhante ao do dióxido de enxofre (SO_2). Esse reagente é muito versátil, sendo utilizado em diversas metodologias de síntese para obtenção de muitos intermediários e produtos químicos das áreas de agroquímica, química fina e farmacêutica. A produção industrial do cloreto de tionila é custosa e necessita de instalações específicas para contenção e manuseio de maneira ambientalmente responsável dos reagentes, produtos e impurezas formadas. São descritas diversas maneiras de se produzir esse reagente em escala industrial e a grande maioria dos processos utiliza óxidos de enxofre em sua produção. Este reagente deve ser manuseado com as devidas precauções, uma vez que a exposição a essa substância pode causar irritações e queimaduras nos olhos, membranas e pele.

palavras-chave: Cloreto de tionila; preparação em escala industrial; óxidos de enxofre.

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