PHOSGENE

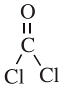
1. Introduction

Phosgene [75-44-5] [75-44-5] (carbonyl chloride, carbon oxychloride, chloroformyl chloride), Cl_2CO, is a colorless, low boiling liquid. The compound was first prepared in 1812 by J. Davy from the photochemical reaction of carbon monoxide and chlorine. Phosgene may be formed at elevated temperatures by oxidation of chlorinated solvents (1–5). Aside from its use as a warfare agent in World War I, phosgene has been used in the preparation of a great variety of chemical intermediates. It is widely used in the preparation of isocyanates which are used in the preparation of polyurethanes (see URETHANE POLYMERS), in the manufacture of polycarbonate, and in the synthesis of chloroformates and carbonates which are used as intermediates in the synthesis of pharmaceuticals and pesticides (see CARBONIC AND CARBONOCHLORIDIC ESTERS). Because of its toxicity, a high level of safety technology has been developed to help ensure the safe handling of phosgene.

2. Properties

Some physical properties of phosgene are listed in Table 1. At room temperature and normal pressure, it is a colorless gas. Impurities may cause discoloration of the product to pale yellow to green. Phosgene has a characteristic odor; the odor of the gas can be detected only briefly at the time of initial exposure. At ca 0.5 ppm in air, the odor has been described as pleasant and similar to that of new-mown hay or cut green corn. At high concentration, the odor may be strong, stifling, and unpleasant. In general, phosgene is soluble in aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, and organic acids and esters. It is removed easily from solvents by heating or sparging with air or nitrogen, but because of its toxicity, great care must be taken to prevent its presence in the atmosphere.

Phosgene is a planar molecule. The interatomic distances are 0.128 nm for the C–O bond, and 0.168 nm for C–Cl (1). The angle Cl–C–Cl is 117°. Infrared, ultraviolet, and Raman spectral properties have been described (7–9).



2.1. Reactions.

Phosgene interacts with many classes of inorganic and organic reagents. The reactions have been described extensively (10). Reaction with sodium metal takes place at room temperature, but reaction with zinc requires warming.

Phosgene is an excellent chlorinating agent. Oxides and sulfides of metals react with phosgene at elevated temperatures, yielding usually very pure chlorides. The reaction of phosgene with cadmium sulfide is a good method for preparing carbonyl sulfide (carbon oxysulfide), COS. The reactions of phosgene with oxides of calcium, magnesium, tin, titanium, tungsten, and zinc have been described (11–18). Chlorination with phosgene of oxides of interest in the nuclear field, especially uranium oxide, plutonium oxide, and thorium oxide, also has been investigated (19–22).

Phosphates and silicates of metals often react with phosgene at elevated temperatures and yield the metal chloride and phosphorus oxychloride or silicon dioxide. The reaction with ferric phosphate at 300–350°C has been proposed as a synthetic method for phosphorus oxychloride, $POCl_3$.

Anhydrous aluminum chloride forms a variety of complexes with phosgene, eg, $Al_2Cl_6{\cdot}5COCl_2$ at low temperatures, $Al_2Cl_6{\cdot}3COCl_2$ at 30°C, and $Al_2Cl_6{\cdot}COCl_2$ above 55°C. Reaction with aluminum bromide yields carbonyl bromide [593-95-3], $COBr_2$, and aluminum chlorobromide, $AlCl_2Br$. Antimony trifluoride with phosgene and chlorine yields carbonyl fluoride (23). Phosgene reacts with sodium fluoride and HCN, yielding phosgene fluorocyanide and carbonyl fluoride [353-50-4] (24).

$$SbF_3 + COCl_2 + Cl_2 \longrightarrow COF_2$$

$$NaF + HCN + COCl_2 \longrightarrow COFCN + COF_2$$

Phosgene reacts slowly with cold water to give CO_2 and HCl and more quickly at higher temperatures (25). In the reaction of gaseous phosgene with water, it is difficult to get the necessary intimate mixing of the gas and water.

$$COCl_2 + H_2O \longrightarrow 2\ HCl + CO_2$$

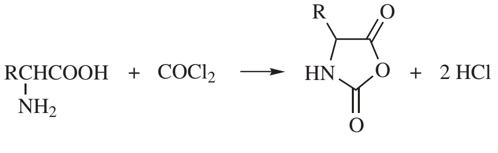
Ammonia reacts vigorously with phosgene. The products are urea, biuret, ammelide (a polymer of urea), cyanuric acid, and sometimes cyamelide (a polymer of cyanic acid). The secondary products probably arise through the very reactive intermediate carbamyl chloride [463-72-9], NH_2COCl (see CYANAMIDES).

Phosgene reacts with a multitude of nitrogen, oxygen, sulfur, and carbon centers. Reaction with primary alkyl and aryl amines yield carbamoyl chlorides which are readily dehydrohalogenated to isocyanates. Secondary amines also form carbamoyl chlorides.

$$RNH_2 + COCl_2 \longrightarrow RNHCOCl + HCl$$

$$RNHCOCl \longrightarrow RN{=}C{=}O + HCl$$

α-Amino acids react readily with phosgene to form oxazolidine-2,5-diones:



Hydrazine reacts with phosgene yielding carbohydrazide:

$$2\,NH_2NH_2 + COCl_2 \longrightarrow NH_2NHCONHNH_2$$

The reaction of phosgene with alcohols yields chloroformates, and with a basic catalyst present, carbonates are formed:

$$ROH + COCl_2 \longrightarrow ROCOCl + HCl$$

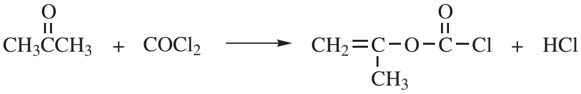
$$ROCOCl + ROH + \text{catalyst} \longrightarrow ROCOOR + HCl$$

This reaction is commercially important because it serves as a basis for the manufacture of polycarbonate.

Carboxylic acids react with phosgene to give acid chlorides (26) (see Carboxylic acids).

$$RCOOH + COCl_2 \longrightarrow RCOCl + CO_2 + HCl$$

Ketones also react with phosgene:

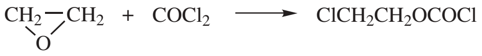


$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + COCl_2 \longrightarrow CH_2{=}\underset{CH_3}{C}{-}O{-}\overset{O}{\overset{\|}{C}}{-}Cl + HCl$$

Amides react with phosgene to yield nitriles (qv).

$$RCONH_2 + COCl_2 \longrightarrow RCN + CO_2 + 2\,HCl$$

Phosgene also can initiate ring opening:



Although $POCl_3$ is the traditional reagent in the Vilsmeier aldehyde synthesis, phosgene may be employed (27–29).

3. Manufacture

Phosgene is manufactured by reaction of carbon monoxide with chlorine over activated carbon. Depending on the quantity needed and availability of the raw materials, numerous variations of the basic synthetic process are being practiced. Continuous processing and a high degree of automation are required for phosgene purification, condensation, and storage. Because of its toxicity, careful and extensive safety procedures and safety equipment are incorporated in plant design and operation. The manufacture of phosgene consists of preparation and purification of carbon monoxide, preparation and purification of chlorine, metering and mixing of reactants, reaction of mixed gases over activated carbon catalyst, purification and condensation of phosgene, and recovery of traces of phosgene to assure worker and environmental safety.

Carbon monoxide (qv) may be manufactured according to standard processes from coke, ie, from coal, or by controlled oxidation of hydrocarbon fuels. A carbon monoxide process must be chosen that yields a gas of the highest possible purity. Noncondensable impurities are particularly objectionable since their presence makes the recovery of phosgene difficult. Water must be removed from the starting gas to preclude hydrochloric acid formation in the phosgene generator. The hydrocarbon and hydrogen content should be minimized because reaction of chlorine with methane or hydrogen could ignite a reaction between chlorine and steel, thereby destroying the equipment. Other impurities might poison the activated carbon catalyst. Sulfides must be excluded since they produce sulfur chlorides which usually are undesirable impurities. The chlorine must be as dry and pure as the carbon monoxide to avoid corrosion of the equipment and decomposition of phosgene by water and other impurities (see CORROSION AND CORROSION CONTROL; HYDROCARBONS).

Activated carbon of high absorptive capacity is suitable for use as a catalyst; it need not be treated with metallic salt or other substances. If starting materials of high purity are employed, excellent and economic catalyst efficiency is obtained.

The phosgene generators employed are relatively simple, tubular heat exchangers that are filled with granulated activated carbon (see CARBON, ACTIVATED CARBON). Because the reaction is rapid and exothermic, efficient heat removal is important. Decomposition of phosgene into its starting materials begins to take place at 200°C. The temperature of the carbon bed in the initial reaction zone of the tubes can reach 400°C, but it rapidly falls to product temperatures of 40–150°C. The reaction is generally run at normal pressure or at a slight excess pressure. A phosgene generation system which monitors the phosgene requirements of a plant and responds by producing only the needed amounts has been developed (30,31).

A flow diagram of the production of phosgene is given in Figure 1. Carbon monoxide and chlorine gas are mixed in equimolecular proportions. A small amount of excess carbon monoxide may be used to ensure complete reaction of the chlorine. The product gases can be condensed leading to liquid phosgene and uncondensed gases, which are then scrubbed for removal of remaining phosgene. Uncondensed gaseous phosgene can be employed for in-line operations. In some cases, phosgene is absorbed into a solvent in a so-called absorption column. The solvent used for the absorption is typically the solvent used in a later process step. The remaining nonabsorbable gas stream is fed to the waste gas treatment system to be freed from phosgene.

3.1. Waste Gas Streams. Several methods of decomposing phosgene in waste gas streams are used. The outlet gas from the phosgene decomposition equipment is continuously monitored for residual phosgene content to ensure complete decomposition.

Decomposition by Caustic Scrubbing. The waste gas stream is led through packed towers where a sodium hydroxide solution is introduced at the top of the towers. Venturi scrubbers can also be used. Makeup sodium hydroxide is added under pH control (32).

Decomposition with Moist Activated Carbon. The waste gas stream is passed through packed activated carbon towers where water is fed at the top of the towers. The water is normally recycled. If the hydrochloric acid concentration in the recycled water exceeds 10%, the decomposition efficiency is greatly reduced. Thus, a sufficient supply of fresh water must be assured and a hydrochloric acid stream continuously taken out (33).

Combustion. The waste gas stream is burnt to convert phosgene to carbon dioxide and HCl. An advantage of this method is that all components of the waste gas, such as CO and solvent, are burnt (34).

4. Analytical and Test Methods

Phosgene in air and in mixture with other gases can be detected by a variety of methods (35). Trace quantities to a lower limit of 0.05 μg/L air can be detected by uv spectroscopy (36). Both ir and gas chromatography have been used extensively to measure phosgene in air at 1 ppb–1 ppm (7,37,38). Special and multiple-column gas-chromatographic methods have been used for more complex mixtures of gases containing phosgene (39–41). High performance liquid chromatography (hplc) methods can also be used and offer detection limits of 5–10 ppb phosgene (42,43). Absolute determination of phosgene at levels below 100 ppb has been reported using pulsed flow coulometry (44). Laser photoacoustic spectroscopy has been used to detect phosgene at ppb levels (45) (see LASERS).

Methods and instruments that are used to monitor phosgene content in air are well developed and have been reviewed (46–48). One detection instrument is a porous tape that measures the concentration of phosgene in air in quantities as small as 6 ppb (49). Fourier transform ir spectrometry techniques have been developed to permit line and area monitoring in the area around phosgene plants (50).

Phosgene dose-indicator badges for personnel exposure monitoring are commercially available and validated (51–52). This is a simple, visually readable, passive sampler based on phosgene indicator paper which is impregnated with a solution of *p*-nitrobenzylpyridine and *N*-benzylaniline. These indicator badges are used at a number of plant sites using phosgene.

Liquid phosgene is assayed by an iodometric method which involves the following reaction (53). The released iodine is titrated with sodium thiosulfate.

$$COCl_2 + 2\,NaI \longrightarrow CO + I_2 + 2\,NaCl$$

The following specifications and standards have been reported (6):

Assay	Percent
$COCl_2$, min	99.0
Cl_2 (free), max	0.1
HCl, max	0.2

5. Storage and Handling

All phosgene containers require a Class A, poison gas label as well as a corrosive label. Phosgene is transported in steel cylinders which conform to rigid safety design specifications. The cylinders undergo special hydrostatic testing at 5.5 MPa (800 psi), and extension rings are incorporated in the cylinders to protect the valves. Phosgene is shipped in cylinders ranging in size from 43 to 909 kg. Careful testing for leaks is required after filling, and a vapor space must be accommodated in the storage vessel; excessive filling with liquid phosgene must be avoided.

Transportation requirements and classifications for phosgene are as follows:

DOT shipping name	phosgene
DOT hazard class	2.3
Reportable quantity (RQ)	yes - 10 lbs (4.5 kg)
DOT labels	poison, corrosive
DOT placards	poison
bill of lading description	phosgene, 2.3, UN1076, RQ (phosgene), inhalation hazard, poison gas and corrosive labels affixed
UN/NA number	UN1076
additional DOT requirements	return of empty containers: residue last contained: phosgene, 2.3, UN1076, RQ (phosgene), inhalation hazard, poison gas and corrosive labels affixed

Because phosgene reacts with water, great care must be taken to prevent contamination with traces of water since this could lead to the development of pressure by hydrogen chloride and carbon dioxide. Wet phosgene is very corrosive; therefore phosgene should never be stored with any quantity of water (4).

6. Health and Safety Factors

The odor threshold for phosgene is ca 0.5–1 ppm, but it varies with individuals and is higher after prolonged exposure (54). Phosgene may irritate eyes, nose, and throat. The permissible exposure TLV by volume in air is 0.1 ppm (55). The TLV refers to the average airborne concentration at which it is believed nearly all workers may be repeatedly exposed on a daily basis without adverse effect. It is a time-weighted average for an 8-h day or a 40-h week and should be used as a guide for control only. The NIOSH REL (ceiling value) is 0.2 ppm for a 15-minute excursion (56). Medical problems and adverse health effects associated with phosgene exposure have been reviewed, and therapy for phosgene poisoning has also been reviewed (57–60).

When phosgene is inhaled, it reacts very little with the aqueous film on the mucous membranes of the upper respiratory tract. Most of it reaches the pulmonary alveoli, where gas exchange occurs. Here phosgene reacts with NH_2, OH, and SH groups of the blood–air barrier. This causes the blood–air barrier to lose its function as a membrane between the blood vessels and the pulmonary alveoli. As a result, blood plasma is able to pass from the blood vessels into the pulmonary alveoli, thereby increasingly disturbing the gas exchange, ie, the normal lung function.

Breathing phosgene causes pulmonary edema which may be characterized by a delayed onset. The onset of pulmonary edema is a function of both concentration and duration. Typically exposure above 50 ppm-minutes can lead to pulmanary edema (60). Exposed persons must be removed immediately from the contaminated area and decontaminated. Rescue workers should wear self-contained breathing apparatus. Injured persons should not be allowed any physical activity, and a physician should be consulted immediately. It is advisable to keep an exposed individual under the observation of a physician for 6–24 hours, depending on the circumstances of exposure. In some instances this can be accomplished at the plant medical facility, or the exposed individual may require hospitalization.

In handling phosgene, extensive safety precautions and procedures are required to prevent exposure to phosgene. The first point is to design the phosgene system to prevent phosgene emissions from the closed equipment. Chemically resistant, high quality materials are used for plant equipment and lines which are inspected regularly. Pumps, which are hermetically sealed to the outside or utilize multiple mechanical seals with buffer fluids, are used for phosgene-containing streams. Stringent requirements are set for the quality and design of phosgene process control equipment, and critical areas have redundant control systems. The second point is to quickly detect leaks and contain or decompose escaped phosgene. This includes such measures as continuous alarm systems to monitor the working atmosphere, systems for decomposing escaped phosgene (eg, steam-ammonia curtains for gaseous emissions), jacketed pipes, and complete containments for phosgene plants (61,62). Vacuum systems are also utilized by both outdoor processes and processes enclosed in a containment building to mitigate phosgene releases. These systems consist of a series of vacuum hoses that can be put near a small leak to draw in escaping phosgene. The phosgene is then sent to a destruction unit. More detailed information on current industrial practices for safely manufacturing or handling phosgene are available through the Chemical Manufacturers Association Phosgene Panel, Washington, DC.

In case of extensive leaks or spills, immediate evacuation upwind of the phosgene source is necessary. Phosgene is 3.4 times as heavy as air and may collect in low lying areas (6). Water should not be used on the source of a phosgene leak because the resulting corrosion enlarges the leak. Suitable personal protective equipment includes respiratory equipment and eye protection. In case of fire, it is essential to cool all phosgene-containing vessels. Leaks of liquid phosgene or phosgene solutions can be effectively combated by covering the phosgene-containing liquid with an absorbent and decomposition agents.

6.1. Waste Disposal.

Because of its low boiling point and high toxicity, measures must be taken to prevent the entrance of phosgene into drains or sewers. If recycle of phosgene is not feasible, phosgene waste can be handled by one of the decomposition methods mentioned above, ie, caustic scrubbing, moist activated carbon towers, or combustion.

7. Uses

Phosgene is an important and widely used intermediate. Practically all phosgene manufacture is captive, ie, it is used in the manufacture of other chemicals within the plant boundary. Only VanDeMark Inc. sells phosgene on the U.S. merchant market. Phosgene manufacturers with captive consumption are BASF, Bayer, Dow, DuPont, GE Plastics, Huntsman/ICI, Lyondell, PPG, Aventis, Twin Lake Chemicals, VanDeMark Inc., and Zeneca. The U.S. demand and use of phosgene for 1998 was 1.41×10^6 metric tons, and for 1999, it is projected to grow to 1.45×10^6 metric tons (63). The primary use of phosgene is the manufacture of polyisocyanates for the polyurethane industry, where over 80% of the phosgene output in the United States is consumed. The manufacture of toluene diisocyanate [1321-38-6] accounts for ca 40% of the phosgene consumption, whereas diisocyanato diphenylmethane [101-68-8] (MDI) and polymeric MDI [9016-87-9] account for ca 40% (see AMINES, AROMATIC–METHYLENEDIANILINE). The polycarbonate industry accounts for ca 13% of the phosgene consumption, and the remaining 7% is used to produce aliphatic diisocyanates, monoisocyanates, chloroformates, agrochemicals, and intermediates for pharmaceuticals and dyestuffs. Although several commercial phosgene-free processes for producing polyisocyanates and polycarbonates have been announced, they are not expected to make large inroads into phosgene demand in the near future (64–68).

Phosgene can be employed in a variety of metal-recovery operations, eg, in the recovery of platinum, uranium, plutonium, and niobium (69–73). Phosgene has been proposed for the manufacture of aluminum chloride, beryllium chloride, and boron trichloride (74–76). Phosgene has been patented as a stabilizer, either by itself or in combination with thionyl chloride, for liquid SO_2 (77).

Phosgene also is used in the production of chloroformates which are intermediates in the production of ore-flotation agents, perfumes (qv), herbicides (qv), and insecticides (see INSECT CONTROL TECHNOLOGY), and especially in the preparation of pharmaceuticals (qv) (78). Chloroalkyl chlorocarbonates have been manufactured as intermediates for pharmaceuticals and pesticides (qv) (79,80). Phosgene also is employed in the manufacture of carbonic esters. Phosgene has been suggested as a starting material for the manufacture of carbon tetrachloride and other chlorinated hydrocarbons (81–85). A number of pesticides have been patented based on the reaction of a thiol or dithiol with phosgene to form thiol chloroformates (86,87). The preparation of aromatic acids using phosgene, and a detailed process for the manufacture of terephthalic acid from toluene and phosgene, have been described (88,89) (see PHTHALIC ACID AND OTHER BENZENEPOLYCARBOXYLIC ACIDS).

An important direct use of phosgene is in the preparation of polymers. Polycarbonate is the most significant and commercially valuable material (see POLYCARBONATES). However, the use of phosgene has been described for other polymer systems, eg, fiber-forming polymeric polyketones and polyureas (90,91).

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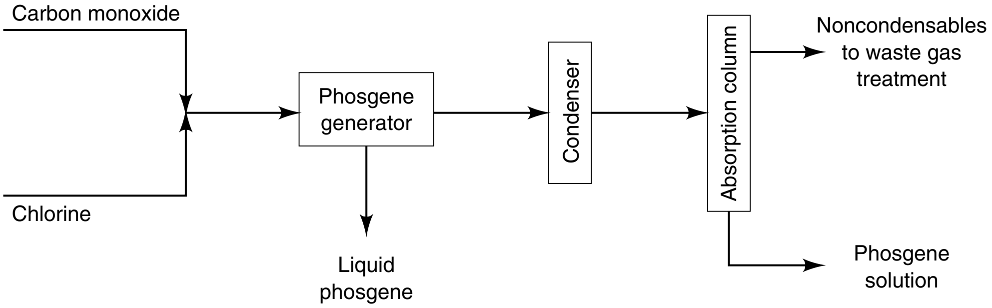

Fig. 1. Manufacture of phosgene from carbon monoxide and chlorine.

Table 1. **Some Physical Properties of Phosgene**[a]

Properties and characteristics	Value
molecular weight	98.92
melting point, °C	−127.84
boiling point, °C[b]	7.48
density at 20°C, g/cm^3	1.387
vapor pressure at 20°C, kPa[c]	161.68
vapor density (air= 1.0)	3.4
critical temperature, °C	182
density at critical point, g/cm^3	0.52
critical pressure, MPa[d]	5.68
latent heat of vaporization, at 7.5°C, J/g[e]	243
molar heat capacity of liquid, at 7.5°C, J/K[e]	100.8
molar heat of formation, kJ[e]	
from elements	218
from CO and Cl_2	108
molar entropy, J/K[e]	
at 7°C	280
25°C	284
surface tension, mN/m(=dyn/cm)	
at 0.0°C	34.6
16.7°C	20.1
34.5°C	17.6
46.1°C	15.9

[a] Ref. 6.

[b] At 101.3 kPa = 1 atm.

[c] To convert kPa to psi, multiply by 0.145.

[d] To convert MPa to psi, multiply by 145.

[e] To convert J to cal, divide by 4.184.