3.0 Properties of Phosgene

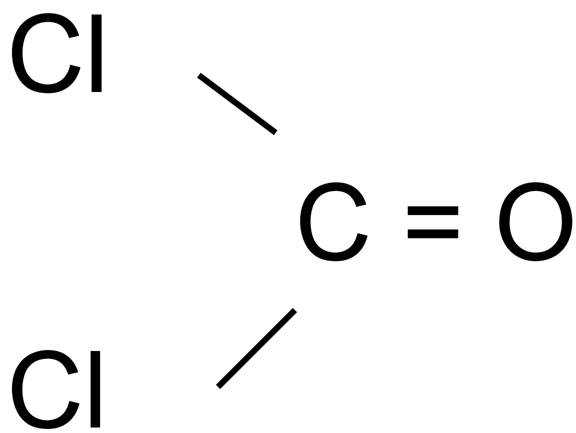
Introduction

The information presented in this section is a general composite of information about the properties of phosgene including the names, formulas, physical properties, reactivity, instability and combustion, commercial chemistry and use.

The information provided in this section should not be considered as a directive or as an industry standard that readers must adopt or follow. Instead, the information is intended to provide helpful ideas and guidance that users may wish to consider in a general sense (See Section 1.1 *Preface and Legal Notice*). Also included is a reference list of useful resources.

Contents

3.1 The Phosgene Molecule



Phosgene (Carbonyl dichloride) was synthesized by the British chemist John Davy (1790–1868) in 1812 by exposing a mixture of carbon monoxide and chlorine to sunlight. He named it "phosgene" in reference of the use of light to promote the reaction; from Greek, phos (light) and gene (born). It gradually became important in the chemical industry as the 19th century progressed, particularly in dye manufacturing. It is also a valued industrial reagent and building block in synthesis of pharmaceuticals and other organic compounds.

3.2 Names

Chemical Name - Phosgene

Chemical Abstract Registry Number - 0000 75-44-5

Other Names:

CARBON DICHLORIDE OXIDE
CARBONE (OXYCHLORURE DE) [FRENCH]
CARBONIC DICHLORIDE
CARBONIO (OSSICLORURCI DI) [ITALIAN]
CARBON OXYCHLORIDE
CARBONYLCHLORID [GERMAN]
CARBONYL CHLORIDE
CARBONYL DICHLORIDE
CG
CHLOROFORMYL CHLORIDE
FOSGEEN (DUTCH)
FOSGEN (POLISH)
FOSGENE (ITALIAN)
FOSGENO (SPANISH)
HSDB 796
KOOLSTOFOXYCHLORIDE (DUTCH)
NCI-C60219
PHOSGEN (GERMAN)
PHOSGENE
RCRA WASTE NUMBER P095

Formula:

$COCl_2$

CCl_2O

3.3 Physical Properties

Grade and Strength - Commercial 100%

Properties & Characteristics

Color and Physical State - At room temperature and pressure, phosgene is a colorless, non-flammable, potentially highly toxic gas. At sufficiently lower temperatures or higher pressures or both, it is a highly toxic colorless liquid.

Note: Phosgene, in the presence of high humidity, water, fog or ammonia, may produce a white cloud.

Property	Value	English Units	Value	Metric Units
Molecular Weight	98.9158	lbm/lbmol	98.9158	g/mol
Critical Temperature	359.33	F	181.85	C
Critical Pressure	822.97462	psia	5.6742E+07	dyne/cm²
Critical Volume	3.04351	ft³/lbmol	190	cm³/mol
Critical Compressibility Factor	0.285		0.285	
Melting Point	-180.4	F	-118	C
Triple Point Temperature	-198.004	F	-127.78	C
Triple Point Pressure	0.0001335	psia	9.20651	dyne/cm²
Normal Boiling Point	46.9	F	8.3	C
Liquid Molar Volume	1.16294	ft³/lbmol	72.59997	cm³/mol
Vapor Pressure	1215	mmHg @ 68 F	1215	mmHg @ 20C
Ideal Gas Heat of Formation	-9.42E+04	BTU/lbmol	-2.189E+12	erg/mol
Ideal Gas Gibbs of Formation	-8.81E+04	BTU/lbmol	-2.0479E+12	erg/mol
Ideal Gas Absolute Entropy	67.81556	BTU/lbmol·R	2.8374E+09	erg/mol·K
Standard Absolute Entropy	67.81556	BTU/lbmol·R	2.8374E+09	erg/mol·K
Standard Heat of Formation	-9.42E+04	BTU/lbmol	-2.189E+12	erg/mol
Standard Gibbs of Formation	-8.81E+04	BTU/lbmol	-2.0479E+12	erg/mol
Enthalpy of Fusion at M.P.	2468.719	BTU/lbmol	5.7384E+10	erg/mol
Heat of Combustion	-7.51114E+04	BTU/lbmol	-1.746E+12	erg/mol
Acentric Factor	0.201309		0.201309	
Radius of Gyration	9.43895E-10	ft	2.877E-08	cm
Solubility Parameter	88.25608	(BTU/ft³)^½	5.3853	(erg/cm³)^½
Dipole Moment	1.16922E-18	esu-cm	1.16922	Debye (D)
Van der Waals Volume	0.5590444	ft³/lbmol	34.89998	cm³/mol
Van der Waals Area	2.53889E+09	ft²/lbmol	5.20E+09	cm²/mol
Refractive Index	1.35609		1.35609	
Flash Point	Unknown	R	Unknown	C
Upper Flammability Limit	Unknown	vol% in air	Unknown	vol% in air
Lower Flammability Limit	Unknown	vol% in air	Unknown	vol% in air
Upper Flammability Temperature	Unknown	R	Unknown	C
Lower Flammability Temperature	Unknown	R	Unknown	C
Auto-ignition Temperature	Unknown	R	Unknown	C
Heat of sublimination	16305	BTU/lbmol	379.001E+09	Erg/mol
Parachor	151.83		151.83	
Dielectric Constant	4.3		4.3	

Odor: At low concentrations, its odor is similar to that of newly mown hay; at high concentrations, its odor can be sharp and suffocating. There may be perceived odors at the lower threshold value but recognition of the odor as phosgene is usually at a higher value.

Odor Threshold: >0.125 ppm (odor perception), >1.5 ppm (recognition of odor)[1]

OSHA Permissible Exposure Limit (by volume in air): 0.1 pmm

ACGIH Threshold Limit Value[2] (by volume in air): 0.1 ppm

3.4 Reactivity, Instability and Combustion Properties

Phosgene is a stable compound at normal ambient temperatures (21°C or 70°F). At temperatures above 250°C (482°F), phosgene decomposes to form mixtures of carbon monoxide (CO), chlorine (Cl_2) carbon dioxide (CO_2) and carbon tetrachloride (CCl_4).

Phosgene reacts slowly with water to form carbon dioxide and hydrochloric acid. Phosgene reacts readily with caustic solution and even more readily with ammonia and ammonia water.

When fighting fires, minimize the reactivity hazards through precautionary measures such as those described in Section 5.0 Emergency Response.

Reactivity hazards exist when attempts are made to neutralize liquid spills because the heat of neutralization increases the rate of vaporization of liquid phosgene. Various techniques for minimizing the rate of vaporization from a liquid spill are listed in Section 5.0 Emergency Response.

3.5 Commercial Chemistry

Phosgene is obtained commercially by passing carbon monoxide and chlorine over activated carbon. The reaction is exothermic, producing heat that must be removed from the reactor.

The formula for the reaction to produce phosgene is:

$$\underset{\text{Carbon Monoxide}}{CO} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow[\text{Carbon}]{\text{Activated}} \underset{\text{Phosgene}}{COCl_2} + \text{Heat}$$

Hydrogen and methane impurities in the carbon monoxide feed gas react with chlorine to produce hydrogen chloride and carbon tetrachloride respectively. The formulas for these two impurity reactions are:

$$H_2 + Cl_2 \longrightarrow 2\,HCl + \text{Heat}$$

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4\,HCl + Heat$$

Hydrogen and methane react with chlorine without catalyst, therefore the reaction can take place in the piping prior to the reactors. Normally, these impurities are at very low concentrations and the impurities formed are not significant. If a high concentration of either impurity exists, these reactions can generate enough heat to melt the pipe. Since chlorine is an oxidizer, and methane, hydrogen and carbon monoxide are fuels, a fire can occur in the pipeline without oxygen. At temperatures above 250°F, chlorine will start reacting with steel, weakening the piping and vessels. At 483°F, chlorine will ignite iron and produce a fire. Detection of these impurity generated reactions can be noticed by a rapid rise in the temperature of the feed gas after the carbon monoxide and chlorine mixing point. The use of high mixing temperature automatic shutdown is a useful method to help eliminate this type of failure.

Carbon tetrachloride and carbon dioxide can also be formed at high temperature by the reaction of two phosgene molecules. In the center of the reaction tubes temperatures are sufficiently hot to cause a small amount of this impurity reaction. The formula for this reaction is:

$$2\,COCl_2 + Heat \longrightarrow CCl_4 + CO_2$$

3.6 Uses

Phosgene is a widely used chemical intermediate, primarily manufactured for the synthesis of isocyanate-based polymers, carbonic acid esters and acid chlorides. It is also used in the manufacture of dyestuffs, some insecticides and pharmaceuticals and in metallurgy.

Phosgene consumption is summarized below:

> Practically all phosgene manufacture is captive; it is used in the manufacture of other chemicals within the plant boundary. Globally, approximately 75% of phosgene is consumed for isocyanates, 20% for polycarbonates, and about 5% for fine chemicals.

TDI Reaction: The overall reaction of toluene diamine with phosgene to form toluene diisocyanate (TDI) is shown below:

$CH_3\text{-}C_6H_3(NH_2)_2$+ **$2\,COCl_2$** ----- **> $CH_3\text{-}C_6H_3(NCO)_2$** + 4 HCl

Toluene diamine	**Phosgene**	**TDI**	HCl

MDI Reaction: The overall reaction of Diaminodiphenyl methane with phosgene to form Methyldiphenyl diisocyanate (MDI) is shown below:

$2(C_6H_4)\text{-}CH_2\text{-}2(NH_2)$ + **$2\ COCl_2$** ----- > **$2(C_6H_4)\text{-}CH_2\text{-}2(NCO)$** + 4 HCl
Diaminodiphenyl methane **Phosgene** **MDI** HCl

Polycarbonate Reaction: The reaction of Bisphenol-A with phosgene gives the very hard and strong polycarbonate plastics that can be molded and extruded.

$x(HO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}OH)$ + x(**$COCl_2$**) - > $2x$ HCl + **$[\text{-}OCO\text{-}O\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}]_x$**
Bisphenol-A **Phosgene** HCl **Polycarbonate**

References

[1]American Chemistry Council Phosgene Panel. Phosgene: Information on Options for First Aid and Medical Treatment. Available at www.americanchemistry.com/phosgenepanel.

[2]American Conference of Governmental Industrial Hygienists, TLV Annual Publication.