3.0 Properties of Phosgene

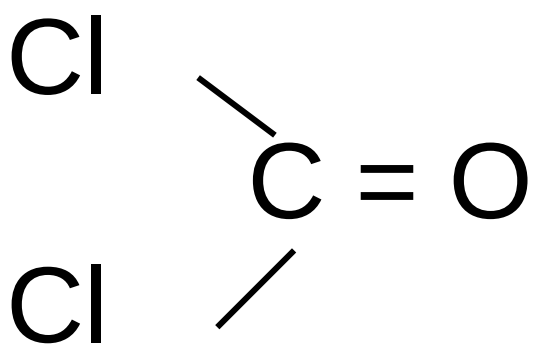
Table of Contents

3.1 Introduction
3.2 Names
3.3 Physical Properties
3.4 Reactivity, Instability and Combustion Properties
3.5 Commercial Chemistry
3.6 Uses

3. Properties of Phosgene

3.1. Introduction

The Phosgene Molecule:



Phos gene (fasjen) n. [[so named (1812) by Sir Humphry DAVY< Gr phos, light+ -gene, born -GEN]] a colorless, volatile, highly poisonous liquid, COC12, prepared by the reaction of carbon monoxide with chlorine in the presence of activated charcoal or, originally, in sunlight; carbonyl chloride: used as a poison gas, in organic synthesis, in making dyes, etc.[1]

3.2. Names

Chemical Name - Phosgene

Chemical Abstract Registry Number - 0000 75-44-5

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Other Names:

CARBON DICHLORIDE OXIDE
CARBONE (OXYCHLORURE DE) [FRENCH]
CARBONIC DICHLORIDE
CARBONIO (OSSICLORURCI DI) [ITALIAN]
CARBON OXYCHLORIDE
CARBON OXYCHLORIDE
CARBONYLCHLORID [GERMAN]
CARBONYL CHLORIDE
CARBONYL DIC"LORIDE
CG
CHLOROFORMYL CHLORIDE

[1] **Excerpted from *Compton's Interactive Encyclopedia.* Copyright (c) 1994, 1995 Compton's NewMedia, Inc. All Rights Reserved.**

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, 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.

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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	5.67E+07	dyne/cm²
Critical Volume	3.04351	ft³/lbmol	190	cm³/mol
Critical Compressibility Factor	0.285		0.285	
Melting Point	-198.004	F	-127.78	C
Triple Point Temperature	-198.004	F	-127.78	C
Triple Point Pressure	0.0001335	psia	9.20651	dyne/cm²
Normal Boiling Point	45.608	F	7.56	C
Liquid Molar Volume	1.12992	ft³/lbmol	70.5389	cm³/mol
Ideal Gas Heat of Formation	-9.42E+04	BTU/lbmol	-2.19E+12	erg/mol
Ideal Gas Gibbs of Formation	-8.81E+04	BTU/lbmol	-2.05E+12	erg/mol
Ideal Gas Absolute Entropy	67.81556	BTU/lbmol·R	2.84E+09	erg/mol·K
Standard Absolute Entropy	67.81556	BTU/lbmol·R	2.84E+09	erg/mol·K
Standard Heat of Formation	-9.42E+04	BTU/lbmol	-2.19E+12	erg/mol
Standard Gibbs of Formation	-8.81E+04	BTU/lbmol	-2.05E+12	erg/mol
Enthalpy of Fusion at M.P.	2468.717	BTU/lbmol	5.74E+10	erg/mol
Heat of Combustion	-7.51E+04	BTU/lbmol	-1.75E+12	erg/mol
Acentric Factor	0.201309		0.201309	
Radius of Gyration	9.44E-10	ft	2.88E-08	cm
Solubility Parameter	92.45383	(BTU/ft³)^½	5.64E+04	(erg/cm³)^½
Dipole Moment	1.17E-18	esu-cm	1.16919	Debye (D)
Van der Waals Volume	0.5590444	ft³/lbmol	34.9	cm³/mol
Van der Waals Area	2.54E+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

Odor Threshold - 0. 12-5.7 ppm[1]. (Threshold varies with individuals and is higher after prolonged exposure).

Odor - Mildly sweet, not an unpleasant odor of musty hay in low concentrations, becoming more pungent in higher concentrations.

Permissible Exposure Limit[2] Threshold Limit Value[3] (by volume in air) - 0.1 ppm.

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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.

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 6.1.4.

Hazardous chemical reactions involving phosgene include the following:

t-Butyl azidoformate - In the formation of tert-butyl azidoformate by the addition of phosgene to alcohols followed by the addition of sodium nitride or hydrazoic acid in the presence of pyridine, reaction of phosgene with the azide can cause the formation of explosive carbazide. To prevent this reaction, completely remove excess phosgene; pass nitrogen into the solution prior to addition of the azide.

Aluminum - Powdered aluminum burns in the vapor of phosgene.

Alcohols - Phosgene reacts with all alcohols; two examples follow:

2,4-Hexadiyne-1,6-diol - The reaction between 2,4-hexadiyne-1,6-diol and phosgene produces 2,4-hexadiyne-1,6-bischloroformate which is a shock-sensitive compound.

Isopropyl Alcohol - The reaction between isopropyl alcohol and phosgene forms isopropyl chloroformate and hydrogen chloride. At temperatures slightly above ambient isopropyl, chloroformate can decompose explosively in the presence of iron salts.

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Secondary Amines - Phosgene may react with secondary amines to form hazardous products.

Potassium - A mixture of potassium and phosgene explodes when subjected to shock.

Sodium - Vapors of sodium and phosgene react with luminescence at about 260°C.

3.5. Commercial Chemistry

Phosgene, $COCl_2$, the acid chloride of carbonic acid, first was made by the action of light on a mixture of carbon monoxide and chlorine (Gr. phos light, genes bom)[1]. In the current process, the mixed gasses are exposed to carbon catalyst. The reaction is exothermic, producing heat that must be removed from the reactor.

The formula for the reaction to produce phosgene is:

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

Textbook of Organic Chemistry, C.R. Noller, W.B. Saunders Company, 1966.

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:

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

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4\,HCl + \text{Heat}$$

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

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rapid rise in the temperature of the feed gas after the carbon monoxide and chlorine mixing point. The use of high mixing temperature automatic shut down 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:

$$2\ COCl_2 + \text{Heat} \longrightarrow CCl_4 + CO_2$$

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. (1,2,3)

1. Great Lakes

2. U.S. Environmental Protection Agency. Health Assessment Document for Phosgene (External Review Draft). EPA/600/8-86/022A. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Research Triangle Park, NC. 1986.

3. M. Sittig. Handbook of Toxic and Hazardous Chemicals and Carcinogens. 2nd ed. Noyes Publications, Park Ridge, NJ. 1985.

Phosgene consumption is summarized below:

> Toluene diisocyanate, 45 percent; MDI and polymeric isocyanates, 38 percent; polycarbonate resins, 12 percent; miscellaneous, including specialty isocyanates, chloroformates and agricultural chemicals, 5 percent. (ChemExpo)

Other uses in the miscellaneous category include certain dye intermediates and preparation of ethyl carbonate, a useful solvent.

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

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

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

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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** HCl **MDI**

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 + **[-OCO-O-C_6H_4-$C(CH_3)_2$-C_6H_4-]**x

Bisphenol-A **Phosgene** HCl **Polycarbonate**

When phosgene reacts with alcohols, the alkyl chloroformate is formed first and further reaction gives the alkyl carbonate.

$COCl_2$ + C_2H_5OH --- > $ClCOOC_2H_5$ + HCl
Phosgene Ethyl chloroformate

$ClCOOC_2H_5$ + C_2H_5OH--- > $OC(OC_2H_5)_2$ + HCl
Ethyl carbonate

Additional Resources

Phosgene. Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Volume 12. John Wiley and Sons, 1978.

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Phosgene. Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A 19, pp. 411 - 42.

Section Title Page I. Properties 411 1.1. Physical Properties 411 1.2. Chemical Properties 412 1.2. I. Reactions with Organic Compounds 412 1.2.2. Reactions with Inorganic Compounds 413 2. Production 413 3. Storage and Transportation 414 4. Quality and Analysis 414 5. Waste-Gas Treatment and Monitoring 415 6. Safety Precautions 415 7. Uses 4l6 8. Economic Aspects 417 9. Toxicology and Occupational Health 417 10. References 419.

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Section Title Page I. Physical Properties 611 2. Chemical Properties 611 3. Production 616 3.I .Phosgenation of Free Amines 617 3.2. Other Phosgenation Procedures 618 3.2. I. Phosgenation of Amine Hydrochlorides 618 3.2.2. Phosgenation of Carbarnate Salts 618 3.2.3. Phosgenation of Ureas 619 3.3. Non-Phosgene Processes.

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