

Formaldehyde

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1. Introduction

Formaldehyde occurs in nature and is formed from organic material by photochemical processes in the atmosphere as long as life continues on earth. Formaldehyde is an important metabolic product in plants and animals (including humans), where it occurs in low but measurable concentrations. It has a pungent odor and is an irritant to the eye, nose, and throat even at a low concentration; the threshold concentration for odor detection is 0.05 – 1 ppm. However, formaldehyde does not cause any chronic damage to human health. Formaldehyde is also formed when organic material is incompletely combusted; therefore, formaldehyde is found in combustion gases from, for example, automotive vehicles, heating plants, gas-fired boilers, and

even in cigarette smoke. Formaldehyde is an important industrial chemical and is employed in the manufacture of many industrial products and consumer articles. More than 50 branches of industry now use formaldehyde, mainly in the form of aqueous solutions and formaldehyde-containing resins. In 1995, the demand for formaldehyde in the three major markets – Northern America, Western Europe, Japan – was 4.1×10^6 t/a [1].

History. Formaldehyde was first synthesized in 1859, when BUTLEROV hydrolyzed methylene acetate and noted the characteristic odor of the resulting solution. In 1867, HOFMANN conclusively identified formaldehyde, which he prepared by passing methanol vapor and air over a heated platinum spiral. This method, but with other catalysts, still constitutes the principal method

of manufacture. The preparation of pure formaldehyde was described later by KÉKULÉ in 1882.

Industrial production of formaldehyde became possible in 1882, when TOLLENS discovered a method of regulating the methanol vapor : air ratio and affecting the yield of the reaction. In 1886 LOEW replaced the platinum spiral catalyst by a more efficient copper gauze. The German firm, Mercklin und Lösekann, started to manufacture and market formaldehyde on a commercial scale in 1889. Another German firm, Hugo Blank, patented the first use of a silver catalyst in 1910.

Industrial development continued from 1900 to 1905, when plant sizes, flow rates, yields, and efficiency were increased. In 1905, Badische Anilin & Soda-Fabrik started to manufacture formaldehyde by a continuous process employing a crystalline silver catalyst. Formaldehyde output was 30 kg/d in the form of an aqueous 30 wt % solution.

The methanol required for the production of formaldehyde was initially obtained from the timber industry by carbonizing wood. The development of the high-pressure synthesis of methanol by Badische Anilin & Soda-Fabrik in 1925 allowed the production of formaldehyde on a true industrial scale.

2. Physical Properties

2.1. Monomeric Formaldehyde

Formaldehyde [50-00-0], CH₂O, *M_r* 30.03, is a colorless gas at ambient temperature that has a pungent, suffocating odor and an irritant action on the eyes and skin.

Formaldehyde liquefies at -19.2 °C, the density of the liquid being 0.8153 g/cm³ at -20 °C and 0.9172 g/cm³ at -80 °C. It solidifies at -118 °C to give a white paste. The liquid and gas polymerize readily at low and ordinary temperatures up to 80 °C. Pure formaldehyde gas does not polymerize between 80 and 100 °C and behaves as an ideal gas. For the UV absorption spectra of formaldehyde, see [2]. Structural information about the formaldehyde molecule is provided by its fluorescence [3], IR [4], RAMAN [5], and microwave spectra [6]. Following are some of the thermodynamic properties of gaseous formaldehyde:

Heat of formation at 25 °C	-115.9 ± 6.3 kJ/mol
Gibbs energy at 25 °C	-109.9 kJ/mol
Entropy at 25 °C	218.8 ± 0.4 kJmol ⁻¹ K ⁻¹
Heat of combustion at 25 °C	-561.5 kJ/mol
Heat of vaporization at -19.2 °C	23.32 kJ/mol
Specific heat capacity at 25 °C, <i>c_p</i>	35.425 Jmol ⁻¹ K ⁻¹
Heat of solution at 23 °C	
in water	-62 kJ/mol
in methanol	-62.8 kJ/mol
in 1-propanol	-59.5 kJ/mol
in 1-butanol	-62.4 kJ/mol
Cubic expansion coefficient	2.83 × 10 ⁻³ K ⁻¹
Specific magnetic susceptibility	-0.62 × 10 ⁶
Vapor density relative to air	1.04

The vapor pressure *p* of liquid formaldehyde has been measured from -109.4 to -22.3 °C [7] and can be calculated for a given temperature *T* (K) from the following equation:

$$p(\text{kPa}) = 10^{[5.0233 - (1429/T) + 1.75 \log T - 0.00637T]}$$

Polymerization in either the gaseous or the liquid state is influenced by wall effects, pressure, traces of humidity, and small quantities of formic acid. Formaldehyde gas obtained by vaporization of paraformaldehyde or more highly polymerized α -polyoxymethylenes, which is ca. 90 – 100 % pure, must be stored at 100 – 150 °C to prevent polymerization. Chemical decomposition is insignificant below 400 °C.

Formaldehyde gas is flammable, its ignition temperature is 430 °C [8]; mixtures with air are explosive. At ca. 20 °C the lower and upper explosive limits of formaldehyde are ca. 7 and 72 vol % (87 and 910 g/m³), respectively [9]. Flammability is particularly high at a formaldehyde concentration of 65 – 70 vol %.

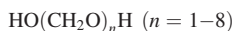
At a low temperature, liquid formaldehyde is miscible in all proportions with nonpolar solvents such as toluene, ether, chloroform, or ethyl acetate. However, solubility decreases with increasing temperature and at room temperature polymerization and volatilization occur, leaving only a small amount of dissolved gas. Solutions of liquid formaldehyde in acetaldehyde behave as ideal solutions [10]. Liquid formaldehyde is slightly miscible with petroleum ether and *p*-cymene [11].

Polar solvents, such as alcohols, amines or acids, either catalyze the polymerization of

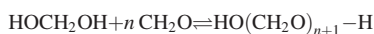
formaldehyde or react with it to form methylol compounds or methylene derivatives.

2.2. Aqueous Solutions

At room temperature, pure aqueous solutions contain formaldehyde in the form of methylene glycol HOCH_2OH [463-57-0] and its oligomers, namely the low molecular mass poly(oxymethylene) glycols with the following structure



Monomeric, physically dissolved formaldehyde is only present in low concentrations of up to 0.1 wt %. The polymerization equilibrium



is catalyzed by acids and is shifted toward the right at lower temperature and/or higher formaldehyde concentrations, and toward the left if the system is heated and/or diluted [12], [13] (see also Section 11.1).

Dissolution of formaldehyde in water is exothermic, the heat of solution (-62 kJ/mol) being virtually independent of the solution concentration [14]. Clear, colorless solutions of formaldehyde in water can exist at a formaldehyde concentration of up to 95 wt %, but the temperature must be raised to 120 °C to obtain the highest concentrations. Concentrated aqueous solutions containing more than 30 wt % formaldehyde become cloudy on storage at room temperature, because larger poly(oxymethylene) glycols ($n \geq 8$) are formed which then precipitate out (the higher the molecular mass of the polymers, the lower is their solubility).

Equilibrium constants have been determined for the physical dissolution of formaldehyde in water and for the reaction of formaldehyde to give methylene glycol and its oligomers [12]. These parameters can be combined with other data to calculate the approximate equilibria at any temperature from 0 to 150 °C and at a formaldehyde concentration of up to 60 wt % [13]. Table 1 gives the calculated oligomer distribution in an aqueous 40 wt % solution of formaldehyde.

A kinetic study of the formation of methylene glycol from dissolved formaldehyde and water

Table 1. Calculated distribution of oligomers of methylene glycol, $\text{HO}(\text{CH}_2\text{O})_n\text{H}$, in an aqueous 40 wt % formaldehyde solution at 35 °C [12]

n	Proportion, %	n	Proportion, %
1	26.80	7	3.89
2	19.36	8	2.50
3	16.38	9	1.59
4	12.33	10	0.99
5	8.70	> 10	1.58
6	5.89		

shows that the reverse reaction is 5×10^3 to 6×10^3 times slower than the forward reaction [15], and that it increases greatly with the acidity of the solution. This means that the distribution of the higher mass oligomers ($n > 3$) does not change rapidly when the temperature is increased or the solution is diluted; the methylene glycol content then rises at the expense of the smaller oligomers ($n = 2$ or 3). In aqueous solutions containing ≤ 2 wt % formaldehyde, formaldehyde is entirely monomeric.

Methylene glycol can be determined by the bisulfite method [16] or by measuring the partial pressure of formaldehyde [17]. Molecular masses and monomer contents can be determined by NMR spectroscopy [13], [18].

The approximate amount of monomeric formaldehyde present as formaldehyde hemiformal and methylene glycol in aqueous solutions containing formaldehyde and methanol, can be calculated from data at 25 – 80 °C [19] by using the following equation:

$$\text{Monomer (mol\%)} = 100 - 12.3\sqrt{F} + (1.44 - 0.0164F)M$$

where F is the formaldehyde concentration (7 – 55 wt %) and M is the methanol concentration (0 – 14 wt %).

The partial pressure p_F of formaldehyde above aqueous solutions has been measured by LEDBURY and BLAIR and computed by WALKER and LACY [20]. The parameter p_F for solutions in which F is in the range 0 – 40 wt % can be calculated with a relative error of 5 – 10 % in the temperature range $T = 273 - 353$ K by using the following equation:

$$p_F(\text{kPa}) = 0.1333F e^{-F^{a_0+a_1/T+a_2/T^2}}$$

$$\alpha = 0.08760 \pm 0.00950$$

$$a_0 = -12.0127 \pm 0.0550$$

$$a_1 = 3451.72 \pm 17.14$$

$$a_2 = 248257.3 \pm 5296.8$$

Table 2. Partial pressure p_F of formaldehyde (kPa) above aqueous formaldehyde solutions

$t, ^\circ\text{C}$	Formaldehyde concentration, wt %								
	1	5	10	15	20	25	30	35	40
5	0.003	0.011	0.016	0.021	0.025	0.028	0.031	0.034	0.037
10	0.005	0.015	0.024	0.031	0.038	0.043	0.049	0.053	0.056
15	0.007	0.022	0.036	0.047	0.057	0.066	0.075	0.083	0.090
20	0.009	0.031	0.052	0.069	0.085	0.099	0.113	0.125	0.137
25	0.013	0.044	0.075	0.101	0.125	0.146	0.167	0.187	0.206
30	0.017	0.061	0.105	0.144	0.180	0.213	0.245	0.275	0.304
35	0.022	0.084	0.147	0.203	0.256	0.305	0.353	0.398	0.442
40	0.028	0.113	0.202	0.284	0.360	0.432	0.502	0.569	0.634
45	0.037	0.151	0.275	0.390	0.499	0.604	0.705	0.803	0.899
50	0.047	0.200	0.371	0.531	0.685	0.833	0.978	1.119	1.258
55	0.059	0.262	0.494	0.715	0.929	1.137	1.341	1.541	1.740
60	0.074	0.340	0.652	0.953	1.247	1.536	1.820	2.101	2.378
65	0.093	0.437	0.852	1.258	1.657	2.053	2.443	2.831	3.218
70	0.114	0.558	1.104	1.645	2.182	2.717	3.250	3.780	4.310

Results of such calculations are given in Table 2 and agree well with the measured values.

Table 3 gives the partial pressures and concentrations of formaldehyde in the liquid and gaseous phases of aqueous formaldehyde solutions. The partial pressures and concentrations were measured at the boiling points of the solutions at a pressure of 101.3 kPa [21].

Aqueous Formaldehyde – Methanol Solutions. Technical-grade formaldehyde solutions contain a small amount of methanol as a result of the incomplete methanol conversion during formaldehyde production. The amount of methanol present depends on the production process employed. The presence of methanol is often

Table 3. Concentration and partial pressure of formaldehyde measured at the boiling points (101.3 kPa) of aqueous formaldehyde solutions [21]

Formaldehyde concentration, wt %		Partial pressure (p_F), kPa
Liquid phase (F_l)	Gaseous phase (F_g)	
3.95	3.68	2.35
8.0	7.3	4.75
12.1	10.6	7.0
15.3	13.2	8.65
20.1	16.95	11.2
25.85	21.45	14.45
30.75	24.9	16.8
35.65	27.4	18.8
42.0	30.5	21.4
47.5	33.1	23.4
49.8	34.0	24.1

desirable in aqueous solutions containing more than 30 wt % formaldehyde because it inhibits the formation of insoluble, higher mass polymers. Methanol concentrations of up to 16 wt % stabilize the formaldehyde.

The approximate *density* ρ (in grams per cubic centimeter) of aqueous formaldehyde solutions containing up to 13 wt % methanol at a temperature of 10 – 70 °C can be calculated by using the following equation [22]:

$$\rho = a + 0.0030(F - b) - 0.0025(M - c) - 10^4[0.055(F - 30) + 5.4](t - 20)$$

where

F = formaldehyde concentration in wt %

M = methanol concentration in wt %

t = temperature in °C

a , b , and c = constants

The following values can be assumed when F is in the range 0 – 48: $a = 1.092$, $b = 30$, and $c = 0$. The corresponding values in the range $F = 48 - 55$ are $a = 1.151$, $b = 50.15$, and $c = 1.61$.

The *boiling points* of pure aqueous solutions containing up to 55 wt % formaldehyde are between 99 and 100 °C at atmospheric pressure [23]. In dilute aqueous solutions, formaldehyde lowers the freezing point of water. If solutions containing more than 25 wt % formaldehyde are cooled, polymer precipitates out before the freezing point is reached. According to NATTA [22], the approximate *refractive index* n_D^{18} of aqueous

30 – 50 wt % formaldehyde solutions containing up to 15 wt % methanol can be calculated from the following equation:

$$n_D^{18} = 1.3295 + 0.00125F + 0.000113M$$

where F and M are wt % concentrations of formaldehyde and methanol, respectively.

In close agreement with measurements of commercial solutions, the *dynamic viscosity* η of aqueous formaldehyde – methanol solutions may be expressed by the following equation [24]:

$$\eta \text{ (mPa} \cdot \text{s)} = 1.28 + 0.039F + 0.05M - 0.024t$$

This equation applies to solutions containing 30 – 50 wt % formaldehyde and 0 – 12 wt % methanol at a temperature t of 25 – 40 °C.

Detailed studies on chemical reactions, vapor–liquid equilibria and calorific properties of systems containing formaldehyde, water, and methanol are available [216–226].

3. Chemical Properties

Formaldehyde is one of the most reactive organic compounds known and, thus, differs greatly from its higher homologues and aliphatic ketones [25], [26]. Only the most important of its wide variety of chemical reactions are treated in this article; others are described in [27]. For a general discussion of the chemical properties of saturated aldehydes, see \rightarrow Aldehydes, Aliphatic.

Decomposition. At 150 °C, formaldehyde undergoes heterogeneous decomposition to form mainly methanol and CO₂ [28]. Above 350 °C, however, it tends to decompose into CO and H₂ [29]. Metals such as platinum [30], copper [31], chromium, and aluminum [32] catalyze the formation of methanol, methyl formate, formic acid, CO₂, and methane.

Polymerization. Anhydrous monomeric formaldehyde cannot be handled commercially. Gaseous formaldehyde polymerizes slowly at temperatures below 100 °C, polymerization being accelerated by traces of polar impurities such as acids, alkalis, or water (see paraformaldehyde, Section 11.1). Thus, in the presence of steam and traces of other polar compounds, the gas is stable at ca. 20 °C only at a pressure of 0.25 – 0.4 kPa,

or at a concentration of up to ca. 0.4 vol % at ca. 20 °C and atmospheric pressure.

Monomeric formaldehyde forms a hydrate with water; this hydrate reacts with further formaldehyde to form polyoxymethylenes (see Section 2.2). Methanol or other stabilizers, such as guanamines [33] or alkylenebis(melamines) [34], are generally added to commercial aqueous formaldehyde solutions (37 – 55 wt %) to inhibit polymerization.

Reduction and Oxidation. Formaldehyde is readily reduced to methanol with hydrogen over a nickel catalyst [27], [35]. For example, formaldehyde is oxidized by nitric acid, potassium permanganate, potassium dichromate, or oxygen to give formic acid or CO₂ and water [27], [36].

In the presence of strong alkalis [37] or when heated in the presence of acids [38], formaldehyde undergoes a Cannizzaro reaction with formation of methanol and formic acid [39]. In the presence of aluminum or magnesium methylate, paraformaldehyde reacts to form methyl formate (Tishchenko reaction) [27].

Addition Reactions. The formation of sparingly water-soluble sodium formaldehyde bisulfite is an important addition reaction of formaldehyde [40]. Hydrocyanic acid reacts with formaldehyde to give glycolonitrile [107-16-4] [27]. Formaldehyde undergoes an acid-catalyzed Prins reaction in which it forms α -hydroxymethylated adducts with olefins [24]. Acetylene undergoes a Reppe addition reaction with formaldehyde [41] to form 2-butyne-1,4-diol [110-65-6]. Strong alkalis or calcium hydroxide convert formaldehyde to a mixture of sugars, in particular hexoses, by a multiple aldol condensation which probably involves a glycolaldehyde intermediate [42], [43]. Mixed aldols are formed with other aldehydes; the product depends on the reaction conditions. Acetaldehyde, for example, reacts with formaldehyde to give pentaerythritol, C(CH₂OH)₄ [115-77-5] (\rightarrow Alcohols, Polyhydric).

Condensation Reactions. Important condensation reactions are the reaction of formaldehyde with amino groups to give Schiff's bases, as well as the Mannich reaction [27]. Amines react with formaldehyde and hydrogen to give

methylamines. Formaldehyde reacts with ammonia to give hexamethylenetetramine, and with ammonium chloride to give monomethylamine, dimethylamine, or trimethylamine and formic acid, depending on the reaction conditions [44]. Reaction of formaldehyde with diketones and ammonia yields imidazoles [45].

Formaldehyde reacts with many compounds to produce methylol ($-\text{CH}_2\text{OH}$) derivatives. It reacts with phenol to give methylolphenol, with urea to give mono-, di-, and trimethylolurea, with melamine to give methylolmelamines, and with organometallic compounds to give metal-substituted methylol compounds [27].

Aromatic compounds such as benzene, aniline, and toluidine combine with formaldehyde to produce the corresponding diphenylmethanes. In the presence of hydrochloric acid and formaldehyde, benzene is chloromethylated to form benzyl chloride [100-44-7] [46]. The possible formation of bis(chloromethyl)ether [542-88-1] from formaldehyde and hydrochloric acid and the toxicity of this compound are reported elsewhere (\rightarrow Ethers, Aliphatic).

Formaldehyde reacts with hydroxylamine, hydrazines, or semicarbazide to produce formaldehyde oxime (which is spontaneously converted to triformoxime), the corresponding hydrazones, and semicarbazone, respectively. Double bonds are also produced when formaldehyde is reacted with malonates or with primary aldehydes or ketones possessing a CH_2 group adjacent to the carbonyl group.

Resin Formation. Formaldehyde condenses with urea, melamine, urethanes, cyanamide, aromatic sulfonamides and amines, and phenols to give a wide range of resins (\rightarrow Amino Resins; \rightarrow Phenolic Resins; \rightarrow Resins, Synthetic).

4. Production

Formaldehyde is produced industrially from methanol [67-56-1] by the following three processes:

1. Partial oxidation and dehydrogenation with air in the presence of silver crystals, steam, and excess methanol at 680 – 720 °C (BASF process, methanol conversion = 97 – 98 %).
2. Partial oxidation and dehydrogenation with air in the presence of crystalline silver or

silver gauze, steam, and excess methanol at 600 – 650 °C [47] (primary conversion of methanol = 77 – 87 %). The conversion is completed by distilling the product and recycling the unreacted methanol.

3. Oxidation only with excess air in the presence of a modified iron – molybdenum – vanadium oxide catalyst at 250 – 400 °C (methanol conversion = 98 – 99 %).

Processes for converting propane, butane [48], ethylene, propylene, butylene [49], or ethers (e.g., dimethyl ether) [50] into formaldehyde are not of major industrial significance for economic reasons. Processes that employ partial hydrogenation of CO [51] or oxidation of methane [52] do not compete with methanol conversion processes because of the lower yields of the former processes.

The specifications of the methanol, used for formaldehyde production according to processes 1 – 3 are listed in Table 4. However, crude aqueous methanol obtained by high- [54], medium-, or low-pressure [55] synthesis can also be used for process 1. This methanol contains low concentrations of inorganic impurities and limited amounts of other organic compounds. The methanol must be first subjected to purification processes and preliminary distillation to remove low-boiling components.

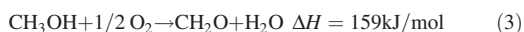
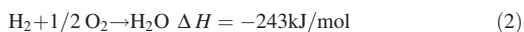
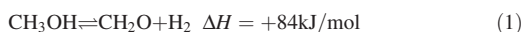
4.1. Silver Catalyst Processes

The silver catalyst processes for converting methanol to formaldehyde are generally carried

Table 4. Specifications of commercial methanol (grade AA) used for the production of formaldehyde [53]

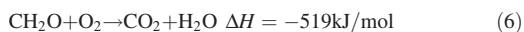
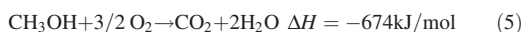
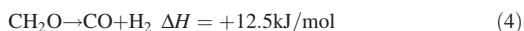
Parameter	Specification
Methanol content	> 99.85 wt %
Relative density, d_4^{20}	0.7928 g/cm ³
Maximum boiling point range	1 °C
Acetone and acetaldehyde content	< 0.003 wt %
Ethanol content	< 0.001 wt %
Volatile iron content	< 2 µg/L
Sulfur content	< 0.0001 wt %
Chlorine content	< 0.0001 wt %
Water content	< 0.15 wt %
pH	7.0
KMnO ₄ test, minimum decolorization time	30 min

out at atmospheric pressure and at 600 – 720 °C. The reaction temperature depends on the excess of methanol in the methanol – air mixture. The composition of the mixture must lie outside the explosive limits. The amount of air that is used is also determined by the catalytic quality of the silver surface. The following main reactions occur during the conversion of methanol to formaldehyde:



The extent to which each of these three reactions occurs, depends on the process data.

Byproducts are also formed in the following secondary reactions:



Other important byproducts are methyl formate, methane, and formic acid.

The endothermic dehydrogenation reaction (1) is highly temperature-dependent, conversion increasing from 50 % at 400 °C to 90 % at 500 °C and to 99 % at 700 °C. The temperature dependence of the equilibrium constant for this reaction K_p is given by

$$\log K_p = (4600/T) - 6.470$$

For detailed thermodynamic data of reactions (1) – (6) see [56]. Kinetic studies with silver on a carrier show that reaction (1) is a first-order reaction [57]. Therefore, the rate of formaldehyde formation is a function of the available oxygen concentration and the oxygen residence time on the catalyst surface:

$$\frac{dc_F}{dt} = kc_O$$

where

c_F = formaldehyde concentration

c_O = oxygen concentration

k = rate constant

t = time

A complete reaction mechanism for the conversion of methanol to formaldehyde over a silver catalyst has not yet been proposed. However, some authors postulate that a change in mechanism occurs at ca. 650 °C [58]. New insight into the reaction mechanism is available from spectroscopic investigations [227–229], which demonstrate the influence of different atomic oxygen species on reaction pathway and selectivity. The synthesis of formaldehyde over a silver catalyst is carried out under strictly adiabatic conditions. Temperature measurements both above and in the silver layer show that sites still containing methanol are separated from sites already containing predominantly formaldehyde by only a few millimeters.

The oxygen in the process air is shared between the exothermic reactions, primarily reaction (2) and, to a lesser extent depending on the process used, the secondary reactions (5) and (6). Thus, the amount of process air controls the desired reaction temperature and the extent to which the endothermic reactions (1) and (4) occur.

Another important factor affecting the yield of formaldehyde and the conversion of methanol, besides the catalyst temperature, is the addition of inert materials to the reactants. Water is added to spent methanol – water-evaporated feed mixtures, and nitrogen is added to air and air – off-gas mixtures, which are recycled to dilute the methanol – oxygen reaction mixture. The throughput per unit of catalyst area provides another way of improving the yield and affecting side reactions. These two methods of process control are discussed in [59].

The theoretical yield of formaldehyde obtained from Reactions (1) – (6) can be calculated from actual composition of the plant off-gas by using the following equation:

$$\text{Yield (mol\%)} = 100 \left[1 + r + \frac{(\% \text{CO}_2) + (\% \text{CO})}{0.528(\% \text{N}_2) + (\% \text{H}_2) - 3(\% \text{CO}_2) - 2(\% \text{CO})} \right]^{-1}$$

Percentages signify concentrations in vol % and r is the ratio of moles of unreacted methanol to moles of formaldehyde produced [60]. The equation takes into account the hydrogen and

oxygen balance and the formation of byproducts.

4.1.1. Complete Conversion of Methanol (BASF Process)

The BASF process for the complete conversion of methanol to formaldehyde is shown schematically in Figure 1 [61]. A mixture of methanol and water is fed into the evaporating column. Fresh process air and, if necessary, recycled off-gas from the last stage of the absorption column enter the column separately [60]. A gaseous mixture of methanol in air is thus formed in which the inert

gas content (nitrogen, water, and CO_2) exceeds the upper explosive limit. A ratio of 60 parts of methanol to 40 parts of water with or without inert gases is desired. The packed evaporator constitutes part of the stripping cycle. The heat required to evaporate the methanol and water is provided by a heat exchanger, which is linked to the first absorption stage of the absorption column [62]. After passing through a demister, the gaseous mixture is superheated with steam and fed to the reactor, where it flows through a 25 – 30 mm thick bed of silver crystals. The crystals have a defined range of particle sizes [63] and rest on a perforated tray, which is covered with a fine corrugated gauze, thus permitting optimum reaction at the surface. The bed is positioned immediately above a water boiler (cooler), which produces superheated steam and simultaneously cools the hot reaction gases to a temperature of 150°C corresponding to that of the pressurized steam (0.5 MPa). The almost dry gas from the gas cooler passes to the first stage of a four-stage packed absorption column, where the gas is cooled and condensed. Formaldehyde is eluted countercurrent to water or to the circulating formaldehyde solutions whose concentrations increase from stage to stage.

The product circulating in the first stage may contain 50 wt % formaldehyde if the temperature of the gas leaving this stage is kept at ca. 75°C ; this temperature provides sufficient evaporation energy for the feed stream in the heat exchanger. The final product contains 40 – 55 wt % formaldehyde, as desired, with an average of 1.3 wt % methanol and 0.01 wt % formic acid. The yield of the formaldehyde process is 89.5 – 90.5 mol %. Some of the off-gas is removed at the end of the fourth stage of the column [60] and is recycled due to its extremely low formaldehyde content (Fig. 1, route indicated by dashed-dotted lines). The residual off-gas is fed to a steam generator, where it is combusted [64] (net calorific value = 1970 kJ/m^3). Prior to combustion the gas contains ca. 4.8 vol % CO_2 , 0.3 vol % CO , and 18.0 vol % H_2 as well as nitrogen, water, methanol, and formaldehyde. The combusted off-gas contains no environmentally harmful substances. The total steam equivalent of the process is 3 t per ton of 100 wt % formaldehyde.

In an alternative procedure to the off-gas recycling process (Fig. 1, dashed lines) the

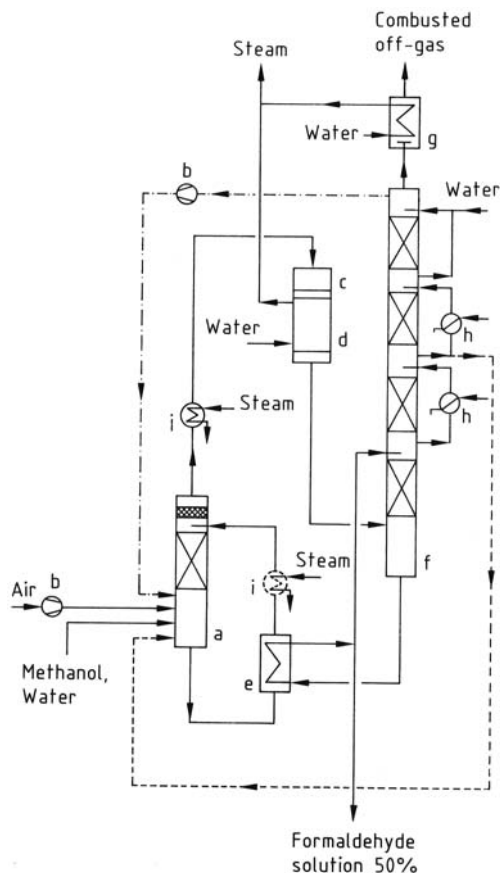


Figure 1. Flowchart of formaldehyde production by the BASF process

a) Evaporator; b) Blower; c) Reactor; d) Boiler; e) Heat exchanger; f) Absorption column; g) Steam generator; h) Cooler; i) Superheater

Recycling schemes: - · - · - off-gas, - - - - formaldehyde solution.

formaldehyde solution from the third or fourth stage of the absorption tower is recycled to the evaporator; a certain amount of steam is used in the evaporation cycle. The resulting vapor is combined with the feed stream to the reactor to obtain an optimal methanol : water ratio [65]. In this case, the temperature of the second stage of the absorption column is ca. 65 °C.

The yields of the two processes are similar and depend on the formaldehyde content of the recycled streams.

The average life time of a catalyst bed depends on impurities such as inorganic materials in the air and methanol feed; poisoning effects caused by some impurities are partially reversible within a few days. The life time of the catalyst is also adversely affected by long exposure to excessively high reaction temperatures and high throughput rates because the silver crystals then become matted and cause an increase in pressure across the catalyst bed. This effect is irreversible and the catalyst bed must be changed after three to four months. The catalyst is regenerated electrolytically.

Since formaldehyde solutions corrode carbon steel, all parts of the manufacturing equipment that are exposed to formaldehyde solutions must be made of a corrosion-resistant alloy, e.g., certain types of stainless steel. Furthermore, tubes that convey water or gases must be made of alloys to protect the silver catalyst against metal poisoning.

If the throughput and reaction temperature have been optimized, the capacity of a formaldehyde plant increases in proportion to the diameter of the reactor. The largest known reactor appears to be that of BASF in the Federal Republic of Germany; it has an overall diameter of 3.2 m and a production capacity of 72 000 t/a (calculated as 100 wt % formaldehyde).

4.1.2. Incomplete Conversion and Distillative Recovery of Methanol

Formaldehyde can be produced by partial oxidation and distillative recovery of methanol. This process is used in numerous companies (e.g., ICI, Borden, and Degussa) [66]. As shown in Figure 2, a feed mixture of pure methanol vapor and freshly blown-in air is generated in an evaporator. The resulting vapor is combined with

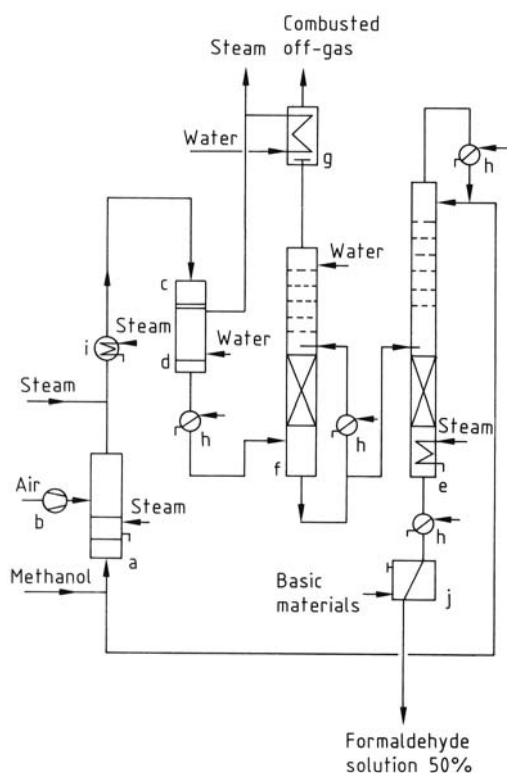


Figure 2. Flowchart of formaldehyde production with recovery of methanol by distillation

a) Evaporator; b) Blower; c) Reactor; d) Boiler; e) Distillation column; f) Absorption column; g) Steam generator; h) Cooler; i) Superheater; j) Anion-exchange unit

steam, subjected to indirect superheating, and then fed into the reactor. The reaction mixture contains excess methanol and steam and is very similar to that used in the BASF process (cf. Section 4.1.1). The vapor passes through a shallow catalyst bed of silver crystals or through layers of silver gauze. Conversion is incomplete and the reaction takes place at 590 – 650 °C, undesirable secondary reactions being suppressed by this comparatively low temperature. Immediately after leaving the catalyst bed, the reaction gases are cooled indirectly with water, thereby generating steam. The remaining heat of reaction is then removed from the gas in a cooler and is fed to the bottom of a formaldehyde absorption column. In the water-cooled section of the column, the bulk of the methanol, water, and formaldehyde separate out. At the top of the column, all the condensable portions of the

remaining formaldehyde and methanol are washed out of the tail gas by countercurrent contact with process water. A 42 wt % formaldehyde solution from the bottom of the absorption column is fed to a distillation column equipped with a steam-based heat exchanger and a reflux condenser. Methanol is recovered at the top of the column and is recycled to the bottom of the evaporator. A product containing up to 55 wt % formaldehyde and less than 1 wt % methanol is taken from the bottom of the distillation column and cooled. The formaldehyde solution is then usually fed into an anion-exchange unit to reduce its formic acid content to the specified level of less than 50 mg/kg.

If 50 – 55 wt % formaldehyde and no more than 1.5 wt % methanol are required in the product, steam addition is restricted and the process employs a larger excess of methanol. The ratio of distilled recycled methanol to fresh methanol then lies in the range 0.25 – 0.5. If a dilute product containing 40 – 44 wt % formaldehyde is desired, the energy-intensive distillation of methanol can be reduced, leading to savings in steam and power as well as reductions in capital cost. The off-gas from the absorption column has a similar composition to that described for the BASF process (in Section 4.1.1). The off-gas is either released into the atmosphere or is combusted to generate steam, thus avoiding environmental problems caused by residual formaldehyde. Alternatively, the tail gas from the top of the absorber can be recycled to the reactor. This inert gas, with additional steam, can reduce the excess methanol needed in the reactor feed, consequently providing a more concentrated product with less expenditure on distillation. The yield of the process is 91 – 92 mol %.

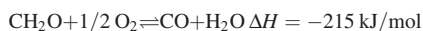
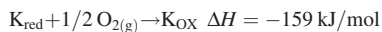
Process variations to increase the incomplete conversion of methanol employ two-stage oxidation systems [67]. The methanol is first partly converted to formaldehyde, using a silver catalyst at a comparatively low temperature (e.g., 600 °C). The reaction gases are subsequently cooled and excess air is added to convert the remaining methanol in a second stage employing either a metal oxide (cf. Section 4.2) or a further silver bed as a catalyst.

Formaldehyde solutions in methanol with a relatively low water content can be produced directly by methanol oxidation and absorption in methanol [68]. Anhydrous alcoholic formal-

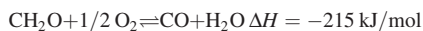
dehyde solutions or alcoholic formaldehyde solutions with a low water content can be obtained by mixing a highly concentrated formaldehyde solution with the alcohol (ROH) and distilling off an alcohol – water mixture with a low formaldehyde content. The formaldehyde occurs in the desired solutions in the form of the hemiacetals RO (CH₂O)_nH.

4.2. Formox Process

In the Formox process, a metal oxide (e.g., iron, molybdenum, or vanadium oxide) is used as a catalyst for the conversion of methanol to formaldehyde. Many such processes have been patented since 1921 [69]. Usually, the oxide mixture has an Mo:Fe atomic ratio of 1.5 – 2.0, small amounts of V₂O₅, CuO, Cr₂O₃, CoO, and P₂O₅ are also present [70]. Special conditions are prescribed for both the process and the activation of the catalyst [71]. The Formox process has been described as a two-step oxidation reaction in the gaseous state (g) which involves an oxidized (K_{OX}) and a reduced (K_{red}) catalyst [72]:



In the temperature range 270 – 400 °C, conversion at atmospheric pressure is virtually complete. However, conversion is temperature-dependent because at >470 °C the following side reaction increases considerably:



The methanol oxidation is inhibited by water vapor. A kinetic study describes the rate of reaction to formaldehyde by a power law kinetic rate expression of the form [230]

$$r = k P_{\text{CH}_3\text{OH}}^x P_{\text{O}_2}^y P_{\text{H}_2\text{O}}^z$$

where $x = 0.94 \pm 0.06$; $y = 0.10 \pm 0.05$ and $z = -0.45 \pm 0.07$. The rate is independent of the formaldehyde partial pressure. The measured activation energy is $98 \pm 6 \text{ kJ/mol}$.

As shown in Figure 3, the methanol feed is passed to a steam-heated evaporator. Freshly

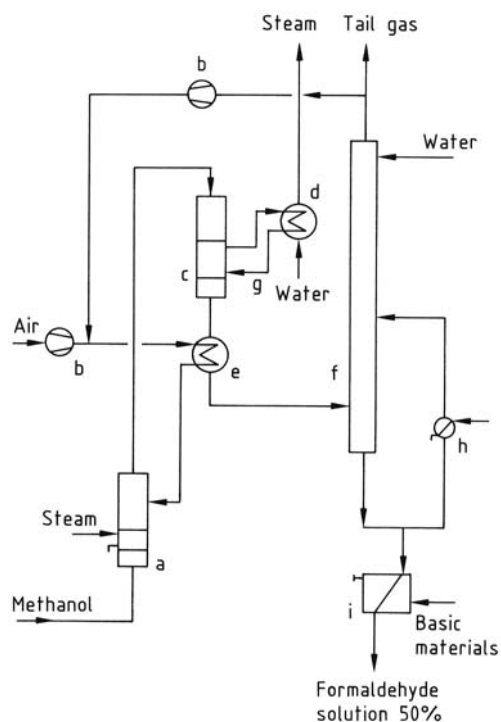


Figure 3. Flowchart of formaldehyde production by the Formox process

a) Evaporator; b) Blower; c) Reactor; d) Boiler; e) Heat exchanger; f) Formaldehyde absorption column; g) Circulation system for heat-transfer oil; h) Cooler; i) Anion-exchange unit

blown-in air and recycled off-gas from the absorption tower are mixed and, if necessary, preheated by means of the product stream in a heat exchanger before being fed into the evaporator. The gaseous feed passes through catalyst-filled tubes in a heat-exchanging reactor. A typical reactor for this process has a shell with a diameter of ca. 2.5 m that contains tubes only 1.0 – 1.5 m in length. A high-boiling heat-transfer oil circulates outside the tubes and removes the heat of reaction from the catalyst in the tubes. The process employs excess air and the temperature is controlled isothermally to a value of ca. 340 °C; steam is simultaneously generated in a boiler. The air – methanol feed must be a flammable mixture, but if the oxygen content is reduced to ca. 10 mol % by partially replacing air with tail gas from the absorption tower, the methanol content in the feed can be increased without forming an explosive mixture [73]. After

leaving the reactor, the gases are cooled to 110 °C in a heat-exchange unit and are passed to the bottom of an absorber column. The formaldehyde concentration is regulated by controlling the amount of process water added at the top of the column. The product is removed from the water-cooled circulation system at the bottom of the absorption column and is fed through an anion-exchange unit to reduce the formic acid content. The final product contains up to 55 wt % formaldehyde and 0.5 – 1.5 wt % methanol. The resultant methanol conversion ranges from 95 – 99 mol % and depends on the selectivity, activity, and spot temperature of the catalyst, the latter being influenced by the heat transfer rate and the throughput rate. The overall plant yield is 88 – 91 mol %.

Well-known processes using the Formox method have been developed by Perstorp/Reichhold (Sweden, United States, Great Britain) [74], [75], Lummus (United States) [76], Montecatini (Italy) [77], and Hiag/Lurgi (Austria) [78].

The tail gas does not burn by itself because it consists essentially of N₂, O₂, and CO₂ with a few percent of combustible components such as dimethyl ether, carbon monoxide, methanol, and formaldehyde. Combustion of Formox tail gas for the purpose of generating steam is not economically justifiable [79]. Two alternative methods of reducing atmospheric emission have been developed. The off-gas can be burned either with additional fuel at a temperature of 700 – 900 °C or in a catalytic incinerator at 450 – 550 °C. However, the latter system employs a heat exchanger and is only thermally self-sufficient if supplementary fuel for start-up is provided and if an abnormal ratio of oxygen : combustible components is used [80].

4.3. Comparison of Process Economics

Considering the economic aspects of the three formaldehyde processes in practice, it becomes obvious that the size of the plant and the cost of methanol are of great importance. Generally, the Formox process proves to be advantageous regarding the attainable formaldehyde yield. However, in comparison with the silver process this process demands a larger plant and higher investment costs. For the purpose of a cost comparison, a study was undertaken based on the cost

Table 5. Comparison of economic factors in formaldehyde production processes [1]

	Complete methanol conversion (BASF process)	Incomplete conversion and methanol recovery	Formox process
Total capital investment, \$ 10 ⁶	6.6	8.6	9.6
Methanol consumption, t/t	1.24	1.22	1.15
Raw materials, \$/t	255	252	227
	Methanol	247	232
	Catalyst and chemicals	5	7
	Byproduct credit (steam)	not mentioned	12
Utilities, \$/t	12	20	13
	LP Steam	3.4	9.5
	Power purchased	3.4	4.3
	Cooling water	2.9	2.8
	Process water	2.4	3.3
Variable costs, \$/t	267	272	240
Direct fixed costs, \$/t	27	29	30
Total allocated fixed costs, \$/t	18	20	21
Total cash cost, \$/t	312	321	291
Depreciation, \$/t	33	43	48
Cost of production, \$/t	345	364	339
Return of total capital investment (ROI), %	33	43	48
Cost of production and ROI, \$/t	378	407	387

of methanol being \$ 200 /t and a plant production capacity of 20,000 t/a of 37 % formaldehyde (calculated 100 %) [1]. Table 5 summarizes the economic data. According to these data the silver process, without the recovery of methanol (cost of formaldehyde \$ 378/t), offers the most favorable production costs, followed by the Formox process (\$ 387/t) and the silver process with recovery (\$ 407/t). The two latter processes produce a product with < 1 % methanol whereas the methanol content in the silver process without recovery lies between 1 – 5 %.

The study takes into consideration the benefit of the production of steam only in the case of the Formox process. If the production of steam is included in the silver process (3 t per tonne CH₂O without and 1.5 t per tonne CH₂O with methanol recovery) better results than demonstrated in Table 5 can be obtained (costs per tonne \$ 24 and \$ 12 lower, respectively). The proven capacity limits of a plant with only one reactor are about 20 000 t/a (calculated 100 %) with the metal oxide process and about 72 000 t/a with the silver process.

The key feature of the BASF process for the production of 50 wt % formaldehyde is a liquid circulation system in which heat from the absorption unit of the plant is transferred to a stripper column to vaporize the methanol – water feed. Therefore, the process produces

excess steam, with simultaneous savings in cooling water.

Plant operation and start-up are simple; the plant can be restarted after a shutdown or after a short breakdown, as long as the temperatures in the stripping cycle remain high. The BASF process has several other advantages. Formaldehyde is obtained from a single pass of the methanol through the catalyst. If a lower formaldehyde concentration is needed (e.g., 40 wt %) the yield can be increased by employing a feedstock of suitably pretreated crude aqueous methanol instead of pure methanol (cf. Section 4.1.1). Deacidification by means of ion exchangers is not necessary. The off-gas does not present any problems because it is burned as a fuel gas in power stations to generate steam or steam and power. The catalyst can be exchanged within 8 – 12 h of plant shutdown to restart and can be regenerated completely with little loss. The plant is compact due to the small volume of gas that is used and the low space requirements; both factors result in low capital investment costs.

Formaldehyde production processes based on incomplete methanol conversion employ a final distillation column to recover the methanol and concentrate the formaldehyde. As shown in Table 5, this means that more steam and cooling water is consumed than in the BASF process. The BASF process has a somewhat lower yield but all

other aspects are roughly comparable. Other distinctive features of the incomplete conversion of methanol are the relatively large amount of direct steam introduced into the feedstock and the lower reaction temperature, which give a somewhat larger amount of hydrogen in the off-gas with a net calorific value of 2140 kJ/m^3 . The additional ion-exchange unit also increases production costs.

The Formox process uses excess air in the methanol feed mixture and requires at least 13 mol of air per mole of methanol. A flammable mixture is used for the catalytic conversion. Even with gas recycling, the process must handle a substantial volume of gas, which is 3 – 3.5 times the gas flow in a silver-catalyzed process. Thus, the equipment must have a large capacity to accommodate the higher gas flow. The main disadvantage of the Formox process is that the off-gas is noncombustible, causing substantial costs in controlling environmental pollution. To reduce air pollution to the levels obtained in the silver-catalyzed processes, a Formox plant must burn the tail gas with sulfur-free fuel, with or without partial regeneration of energy by means of steam production. Advantages of the process are its very low reaction temperature, which permits high catalyst selectivity, and the very simple method of steam generation. All these aspects mean in easily controlled process. Plants based on this technology can be very small with annual capacities of a few thousand tons. As a result, plants employing Formox methanol oxidation are most commonly encountered throughout the world. However, if higher capacities are required and a small number of reactors must be arranged in parallel, the economic data favor the processes employing a silver catalyst.

Although approximately 70% of existing plants use the silver process, in the 1990s new plant contracts have been dominated by the metal oxide technology [1].

4.4. Distillation of Aqueous Formaldehyde Solutions

Since formaldehyde polymerizes in aqueous solutions, the monomer content and thus the vapor pressure of formaldehyde during distillation are determined by the kinetics of the associated reactions.

Vacuum distillation produces a more concentrated bottom product and can be carried out at a low temperature, an extremely low vapor pressure, and an acid pH value of 3 – 3.4 [81]. However, the distillation rates are low, making this procedure uneconomical.

High-pressure distillation at 0.4 – 0.5 MPa and above $130 \text{ }^\circ\text{C}$ with long columns produces a relatively concentrated overhead product. Efficiency is high, but yields are limited due to the formation of methanol and formic acid via the Cannizzaro reaction [82].

If formaldehyde solutions are subjected to slow *distillation at atmospheric pressure* without refluxing, the distillate has a lower formaldehyde content than the bottom product [21]. If the condensate is refluxed, the ratio of condensate (reflux) to distillate determines the formaldehyde content of the distillate removed [81].

In the case of aqueous formaldehyde solutions that contain methanol, a virtually methanol-free product can be obtained by using distillation columns with a large number of plates and a relatively high reflux ratio. The product is taken from the bottom of the column [83].

4.5. Preparation of Liquid Monomeric Formaldehyde

Two methods have been described for the preparation of liquid monomeric formaldehyde from paraformaldehyde, the first was developed by F. WALKER [11] and the second by R. SPENCE [84]. In Walker's method, liquid formaldehyde is prepared by vaporizing alkali-precipitated α -polyoxymethylene. The resultant vapor is then condensed and the crude liquid condensate is redistilled. The process is performed in an apparatus made of Pyrex glass. A vaporizing tube is charged to about one-half its height with the polymer. The thoroughly dried system is then flushed with dry nitrogen. The vaporizing tube is heated to $150 \text{ }^\circ\text{C}$ in an oil bath and the condensing tube is chilled in a bath of solid carbon dioxide and methanol. The polymer is vaporized in a slow stream of nitrogen by gradually raising the temperature. Formation of polymer on the tube walls is minimized by winding wire round the tubes and heating with electricity. The crude liquid product, which is opalescent due to

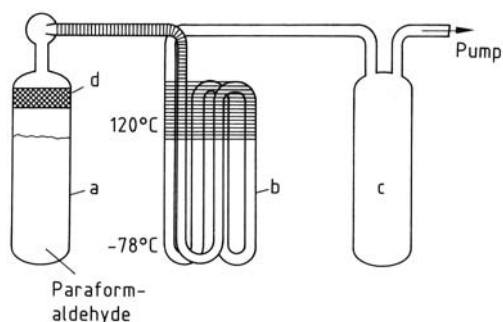


Figure 4. Apparatus for the preparation of liquid monomeric formaldehyde

a) Distillation flask; b) Glass tube with hairpin turns; c) Condenser; d) Glass wool

precipitated polymer, is then distilled in a slow current of nitrogen.

According to the method of SPENCE, paraformaldehyde is dried over sulfuric acid in a vacuum desiccator and introduced into a distillation flask. This flask is connected to a glass condenser via glass tubes with relatively long hairpin turns designed to separate traces of water (Fig. 4). The system is first evacuated by means of a mercury diffusion pump, and the distillation flask is then heated to 110 °C in an oil bath to remove traces of oxygen. The distillate is heated electrically to 120 °C when it flows through the upper parts of the hairpin turns; in the lower parts of the loops, it is cooled to -78 °C by means of a cooling bath. After the valve to the pump is shut and the condenser flask is cooled in liquid air, a colorless solid product condenses. The inlet and outlet tubes of the condenser flask are then sealed with a flame. The contents of the condensing flask liquefy when carefully warmed. The procedure can be repeated to obtain an even purer substance. The liquid formaldehyde that is prepared does not polymerize readily and, when vaporized, leaves only very small traces of polymeric product.

5. Environmental Protection

As already stated, formaldehyde is ubiquitously present in the atmosphere [85]. It is released into the atmosphere as a result of the combustion, degradation, and photochemical decomposition of organic materials. Formaldehyde is also

continuously degraded to carbon dioxide in processes that are influenced by sunlight and by nitrogen oxides. Formaldehyde washed out of the air by rain is degraded by bacteria (e.g., *Escherichia coli*, *Pseudomonas fluorescens*) to form carbon dioxide and water [86].

The major source of atmospheric formaldehyde is the photochemical oxidation and incomplete combustion of hydrocarbons (i.e., methane or other gases, wood, coal, oil, tobacco, and gasoline). Accordingly, formaldehyde is a component of car and aircraft exhaust fumes and is present in considerable amounts in off-gases from heating plants and incinerators. The main emission sources of formaldehyde are summarized in Table 6.

The formaldehyde in the exhaust gases of motor vehicles is produced due to incomplete combustion of motor fuel. Formaldehyde may be produced directly or indirectly. In the indirect route, the unconverted hydrocarbons undergo subsequent photochemical decomposition in the atmosphere to produce formaldehyde as an intermediate [88]. The concentration of formaldehyde is higher above densely populated regions than above the oceans as shown in Table 7 [89]. According to a 1976 report of the EPA [89], the proportions of formaldehyde in ambient air are

Table 6. Sources emitting formaldehyde into the atmosphere [87]

Emission source	Formaldehyde level
Natural gas combustion	
Home appliances and industrial equipment	2400 – 58 800 µg/m ³
Power plants	15 000 µg/m ³
Industrial plants	30 000 µg/m ³
Fuel-oil combustion	0.0 – 1.2 kg/barrel oil
Coal combustion	
Bituminous	< 0.005 – 1.0 g/kg coal
Anthracite	0.5 g/kg coal
Power plant, industrial, and commercial combustion	2.5 mg/kg coal
Refuse incinerators	
Municipal	0.3 – 0.4 g/kg refuse
Small domestic	0.03 – 6.4 g/kg refuse
Backyard (garden refuse)	up to 11.6 g/kg refuse
Oil refineries	
Catalytic cracking units	4.27 kg/barrel oil
Thermoform units	2.7 kg/barrel oil
Automotive sources	
Automobiles	0.2 – 1.6 g/L fuel
Diesel engines	0.6 – 1.3 g/L fuel
Aircraft	0.3 – 0.5 g/L fuel

Table 7. Geographical distribution of formaldehyde in ambient air

Location	Formaldehyde concentration (max.), ppm*
Air above the oceans	0.005
Air above land	0.012
Air in German cities	
normal circumstances	0.016
high traffic density	0.056
Air in Los Angeles (before the law on catalytic combustion of exhaust gases came into effect)	0.165

* 1 ppm = 1.2 mg/m³

derived from the main emission sources as follows:

Exhaust gases from motor vehicles and airplanes (direct production)	53 – 63 %
Photochemical reactions (derived mainly from hydrocarbons in exhaust gases)	19 – 32 %
Heating plants, incinerators, etc.	13 – 15 %
Petroleum refineries	1 – 2 %
Formaldehyde production plants	1 %

Formaldehyde in confined areas comes from the following sources:

1. Smoking of cigarettes and tobacco products [88], [90], [91]
2. Urea-, melamine-, and phenol-formaldehyde resins in particle board and plywood furniture
3. Urea – formaldehyde foam insulation
4. Open fireplaces, especially gas fires and stoves
5. Disinfectants and sterilization of large surfaces (e.g., hospital floors)

Sources generating formaldehyde must be differentiated into those which release formaldehyde for a defined period, cases (1), (4), and (5) and those which release formaldehyde gas continuously, i.e., decomposition of resins as in cases (2) and (3). Many regulations have been issued to limit pollution of the atmosphere with formaldehyde in both general and special applications [92]. Protection against pollution of the environment with formaldehyde must be enforced with due attention to its sources.

The most effective limitation of atmospheric pollution with formaldehyde is the strict observation of the maximum allowable concentration indoors and outdoors. A maximum workplace

concentration of 0.5 ppm (0.6 mg/m³) has, for example, been established in the Federal Republic of Germany [93]. Other limit values and guide values have been specified for formaldehyde levels in outdoor and indoor air. Emission limits for stationary installations have also been established and regulations for specific products have been formulated. Table 8 gives a survey of regulations valid in some countries of the Western world in 1987.

In the Federal Republic of Germany formaldehyde levels and emissions are subjected to stringent regulations. Plants operating with formaldehyde must conform to the plant emission regulations introduced in 1974 which limit formaldehyde in off-gases to a maximum of 20 mg/m³ for mass flow rates of 0.1 kg/h or more [94]. This presupposes a closed handling procedure. For example, industrial filling and transfer of formaldehyde solutions is carried out by using pressure compensation between communicating vessels. Discharge of formaldehyde into wastewater in Germany is regulated by law since it endangers water and is toxic to small animals [95]. Formaldehyde is, however, readily degraded by bacteria in nonsterile, natural water [96].

A maximum limit of 0.1 ppm formaldehyde in indoor living and recreation areas has been recommended by the BGA (German Federal Health Office) [97]. To avoid unacceptable formaldehyde concentrations in room air, the German Institute for Structural Engineering has issued guidelines for classifying particle board into emission categories E1, E2, and E3, class E3 having the highest emission [98]. The lowest class (E1) is allowed a maximum formaldehyde emission of 0.1 ppm and a maximum formaldehyde content of 10 mg per 100 g of absolutely dry board (as measured by the DIN EN-120 perforator method) [99]. Furthermore, the uses and applications of urea – formaldehyde foams, which are used to some extent for the heat insulation of cavity walls, have been controlled by DIN 18 159 [99] since 1978. No formaldehyde emission is permitted after the construction has dried.

Cigarette smoke contains 57 – 115 ppm of formaldehyde and up to 1.7 mg of formaldehyde can be generated while one cigarette is smoked. If five cigarettes are smoked in a 30 m³ room, with a low air-change rate of 0.1 (i.e., 10 %) per hour, the formaldehyde concentration reaches 0.23 ppm [88], [91].

Table 8. International regulations restricting formaldehyde levels

Country	Emission limit		Product-specific regulations
	Outdoor air, ppm	Indoor air, ppm	
Canada		0.1 (1982)	Urea – formaldehyde (UF) foam insulation prohibited. Voluntary program of particle board manufacturers to reduce emission, no upper limit. Registration of infection control agents
Denmark		0.12 (1982)	Guidelines for particle board: max. 10 mg/100 g of absolutely dry board (perforator value). Guidelines for furniture and in situ UF foam. Cosmetic regulations. Prohibited for disinfecting bricks, wood, and textiles if there is contact with food
Federal Republic of Germany	0.02 (MIK _D , 1966) ^a 0.06 (MIK _K , 1966) ^b	0.1 (1977)	Particle board classification. Guidelines (GefStoffV, Gefahrstoffverordnung) for wood and furniture: upper emission limit 0.1 ppm, corresponding to 10 mg/100 mg of absolutely dry board (perforator value); detergents, cleaning agents, and conditioners: upper limit 0.2 %; textiles: compulsory labeling if formaldehyde content >0.15 %. Guidelines for in situ UF foam: upper limit 0.1 ppm. Cosmetic regulations
Finland		0.12 0.24 for pre 1983 buildings (1983)	Upper limit for particle board: 50 mg/100 g absolutely dry board (perforator value). Prohibited as an additive in hairsprays and antiperspirants. Guidelines for cosmetics, but as yet (1987) no EEC directives
Great Britain			Upper limit for particle board: 70 mg/100 g of absolutely dry board (perforator value)
Italy		0.1 (1983)	Cosmetic regulations (July 1985)
Japan			Prohibited as an additive in foods, food packaging, and paints. Guidelines for particle board, textiles, wall coverings, and adhesives
The Netherlands		0.1 obligatory for schools and rented accommodation (1978)	Particle board quality standard on a voluntary basis: upper limit 10 mg/100 g of absolutely dry board (perforator value). Particle board regulations in preparation
Sweden		0.4 – 0.7 (1977)	Particle board and plywood quality standards: upper limit 40 mg/100 g of absolutely dry board (perforator value)
Switzerland		0.2 (introduced 1984, came into force 1986)	Particle board quality standard on a voluntary basis: upper limit 10 mg/100 g of absolutely dry board (perforator value, Oct. 1985); quality symbol “Lignum CH 10”
Spain			Regulations for in situ UF foam (1984): upper limit 1000 µg/m ³ = 0.8 ppm, 7 days after installation; 500 µg/m ³ = 0.4 ppm, 30 days after installation
United States		0.4 (Minnesota, 1984) ^c 0.4 (Wisconsin, 1982) ^c	UF foam insulation prohibited in Massachusetts, Connecticut, and New Hampshire; upper limit for existing UF-insulated houses in Massachusetts 0.1 ppm (1986). FDA limit for nailhardening preparations: 5 %. Department of housing and urban development (HUD) guidelines for emission from particleboard and plywood for the construction of mobile houses: upper limit 0.3 ppm.

^aMIK_D= Maximum allowable concentration for constant immission (mean annual value).^bMIK_K= Maximum allowable concentration for short-term immission (30 min or 24 h).^cReplaced by HUD product standards, 1985.

The best protection against accumulation of formaldehyde in confined spaces is, however, proper ventilation. The strong smell of formaldehyde is perceptible at low concentration and thus provides adequate warning of its presence. If all manufacturing and application regulations are strictly observed, possible emission of formaldehyde from consumer products is very low and will not therefore constitute a human health hazard.

Formaldehyde concentrations in cosmetic products have been limited since 1977, they must be appropriately labeled if they contain > 0.05 wt % formaldehyde [100]. Below this level, formaldehyde does not cause allergic reactions even in sensitive subjects.

6. Quality Specifications and Analysis

6.1. Quality Specifications

Formaldehyde is commercially available primarily in the form of an aqueous (generally 30 – 55 wt %) solution, and in solid form as paraformaldehyde or trioxane (cf. Chap. 11). Formaldehyde solutions contain 0.5 – 12 wt % methanol or other added stabilizers (see Chap. 7). They have a pH of 2.5 – 3.5, the acid reaction being due to the presence of formic acid, formed from formaldehyde by the Cannizzaro reaction. The solutions can be temporarily neutralized with ion exchangers. Typical product specifications for formulations on the European market are listed in Table 9. Other manufacturers' specifications are described in [102–108].

6.2. Analysis

The chemical reactivity of formaldehyde provides a wide range of potential methods for its qualitative and quantitative determination in solutions and in the air.

Qualitative Methods. Qualitative detection of formaldehyde is primarily by colorimetric methods, e.g., [109], [110]. Schiff's fuchsin – bisulfite reagent is a general reagent used for detecting aldehydes. In the presence of strong acids, it reacts with formaldehyde to form a specific bluish violet dye. The detection limit is ca. 1 mL/m³. Further qualitative detection methods are described in [111].

Quantitative Methods. Formaldehyde can be quantitatively determined by either physical or chemical methods.

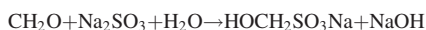
Physical Methods. Quantitative determination of pure aqueous solutions of formaldehyde can be carried out rapidly by measuring their specific gravity [27]. Gas chromatography [112], [113] and high-pressure liquid chromatography (HPLC) [114–116] can also be used for direct determination.

Chemical Methods. The most important chemical methods for determining formaldehyde are summarized in [111]. The sodium sulfite method is most commonly used. This method was developed by LEMMÉ [117] and was subsequently improved by SEYEWETZ and GIBELLO [118], STADTLER [119], and others. It is based on

Table 9. Typical specifications of commercial formaldehyde solutions [101]

Formaldehyde content, wt %	Methanol content (max), wt %	Formic acid content (max), mg/kg	Iron content (max), mg/kg	Density		Added Stabilizer
				t, °C	g/mL	
30	1.5	150	0.8	20	1.086 – 1.090	
37	1.8	200	1	20	1.107 – 1.112	
37	8 – 12	200	1	20	1.082 – 1.093	Methanol
37	1.8	200	1	20	1.108 – 1.112	Isophthalobisguanamine, 100 mg/kg
50	2.0	200	1	55	1.126 – 1.129	
50	2.0	200	1	40	1.135 – 1.138	Isophthalobisguanamine, 200 mg/kg

the quantitative liberation of sodium hydroxide produced when formaldehyde reacts with excess sodium sulfite:



The stoichiometrically formed sodium hydroxide is determined by titration with an acid [27].

Formaldehyde in air can be determined down to concentrations in the $\mu\text{L}/\text{m}^3$ range with the aid of gas sampling apparatus [120], [121]. In this procedure, formaldehyde is absorbed from a defined volume of air by a wash liquid and is determined quantitatively by a suitable method. The quantitative determination of formaldehyde in air by the sulfite/pararosaniline method is described in [122].

A suitable way of checking the workplace concentration of formaldehyde is to take a relevant sample to determine the exposure of a particular person and to use this in combination with the pararosaniline method. The liquid test solution is transported in a leakproof wash bottle [111]. A commercial sampling tube [123], [124] can also be used, in which the formaldehyde is converted to 3-benzylloxazolidine during sampling. Evaluation is carried out by gas chromatography.

Continuous measurements are necessary to determine peak exposures, e.g., by the pararosaniline method as described in [125].

7. Storage and Transportation

With a decrease in temperature and/or an increase in concentration, aqueous formaldehyde solutions tend to precipitate paraformaldehyde. On the other hand, as the temperature increases, so does the tendency to form formic acid. Therefore, an appropriate storage temperature must be maintained (Table 10). The addition of stabilizers is also advisable (e.g., methanol, ethanol, propanol, or butanol). However, these alcohols can be used only if they do not interfere with further processing, or if they can be separated off; otherwise, effluent problems may be encountered.

The many compounds used for stabilizing formaldehyde solutions include urea [126], melamine [127], hydrazine hydrate [128], methylcellulose [129], guanamines [130], and

Table 10. Storage temperatures for commercial formaldehyde solutions

Formaldehyde content, wt %	Methanol content, wt %	Storage temperature, °C
30	≤ 1	7 – 10
37	< 1	35
37	7	21
37	10 – 12	6 – 7
50	1 – 2	45*
50	1 – 2	60 – 65

*Stabilized with 200 mg/kg of isophthalobisguanamine

bismelamines [33]. For example, by adding as little as 100 mg of isophthalobisguanamine [5118-80-9] per kilogram of solution, a 40-wt % formaldehyde solution can be stored for at least 100 d at 17 °C without precipitation of paraformaldehyde, and a 50-wt % formaldehyde solution can be stored for at least 100 d at 40 °C [32].

Formaldehyde can be stored and transported in containers made of stainless steel, aluminum, enamel, or polyester resin. Iron containers lined with epoxide resin or plastic may also be used, although stainless steel containers are preferred, particularly for higher formaldehyde concentrations. Unprotected vessels of iron, copper, nickel, and zinc alloys must not be used.

The flash point of formaldehyde solutions is in the range 55 – 85 °C, depending on their concentration and methanol content. According to German regulations for hazardous substances (Gefahrstoffverordnung, Appendix 6) and Appendix 1 of the EEC guidelines for hazardous substances, aqueous formaldehyde solutions used as working materials that contain ≥ 1 wt % of formaldehyde must be appropriately labeled. The hazard classifications for the transport of aqueous formaldehyde solutions with a flash point between 21 and 55 °C containing > 5 wt % formaldehyde and < 35 wt % methanol are as follows [131]:

GGVS/GGVE, ADR/RID CFR	Class 8, number 63 c 49: 172.01 flammable liquid
IMDG Code (GGVSee)	Class 3.3
UN No.	1198

Formaldehyde solutions with a flash point > 61 °C and aqueous formaldehyde solutions with a flash point > 55 °C that contain > 5 wt % formaldehyde and < 35 wt % methanol are

classified as follows:

GGVS/GGVE, ADR/RID CFR	Class 8, number 63 c 49: 172.01 combustible liquid
IMDG Code (GGVSee)	Class 9
UN No.	2209

8. Uses

Formaldehyde is one of the most versatile chemicals and is employed by the chemical and other industries to produce a virtually unlimited number of indispensable products used in daily life [132].

Resins. The largest amounts of formaldehyde are used for producing condensates (i.e., resins) with urea, melamine, and phenol and, to a small extent, with their derivatives (see also → Amino Resins; → Phenolic Resins; → Resins, Synthetic). The main part of these resins is used for the production of adhesives and impregnating resins, which are employed for manufacturing particle boards, plywood, and furniture. These condensates are also employed for the production of curable molding materials; as raw materials for surface coating and as controlled-release nitrogen fertilizers. They are used as auxiliaries in the textile, leather, rubber, and cement industries. Further uses include binders for foundry sand, rockwool and glasswool mats in insulating materials, abrasive paper, and brake linings. A very small amount of urea – formaldehyde condensates are used in the manufacture of foamed resins (→ Foamed Plastics, → Foamed Plastics, → Foamed Plastics) that have applications in the mining sector and in the insulating of buildings.

Use as an Intermediate. About 40 % of the total formaldehyde production is used as an intermediate for synthesizing other chemical compounds, many of which are discussed under separate keywords. In this respect, formaldehyde is irreplaceable as a C₁ building block. It is, for example, used to synthesize 1,4-butanediol [110-63-4], trimethylolpropane [77-99-6], and neopentyl glycol [126-30-7], which are employed in the manufacture of polyurethane and polyester

plastics, synthetic resin coatings, synthetic lubricating oils, and plasticizers. Other compounds produced from formaldehyde include pentaerythritol [115-77-5] (employed chiefly in raw materials for surface coatings and in permissible explosives) and hexamethylenetetramine [100-97-0] used as a cross-linking agent for phenol – formaldehyde condensates and permissible explosives).

The complexing agents nitrilotriacetic acid [139-13-9] (NTA) and ethylenediaminetetraacetic acid [60-00-4] (EDTA) are derived from formaldehyde and are components of modern detergents. The demand for formaldehyde for the production of 4,4'-diphenylmethane diisocyanate [101-68-8] (MDI) is steadily increasing. This compound is a constituent of polyurethanes used in the production of soft and rigid foams and, more recently, as an adhesive and for bonding particle boards.

The so-called polyacetal plastics (→ Polyoxymethylenes) produced by polymerization of formaldehyde are increasingly being incorporated into automobiles to reduce their weight and, hence, fuel consumption. They are also used for manufacturing important functional components of audio and video electronics equipment [232].

Formaldehyde is also a building block for products used to manufacture dyes, tanning agents, dispersion and plastics precursors, extraction agents, crop protection agents, animal feeds, perfumes, vitamins, flavorings, and drugs.

Direct Use. Only a very small amount of formaldehyde is used directly without further processing. In the Federal Republic of Germany, ca. 8000 t/a are used in this way, which corresponds to ca. 1.5 % of total production. It is used directly as a corrosion inhibitor, in the metal industry as an aid in mirror finishing and electroplating, in the electrodeposition of printed circuits, and in the photographic industry for film development. However, formaldehyde as such is used mainly for preservation and disinfection, for example, in medicine for disinfecting hospital wards, preserving specimens, and as a disinfectant against athlete's foot (→ Disinfectants).

Modern hygiene requires preservatives and disinfectants to prevent the growth of microorganisms which can produce substances

that may be extremely harmful to man. As an antimicrobial agent, formaldehyde displays very few side effects, but has a broad spectrum of action. All alternative agents have unpleasant or even dangerous side effects. Moreover, their toxicity has not been as thoroughly investigated as that of formaldehyde, and their spectrum of action is limited (i.e., they do not provide comprehensive disinfectant protection). Another advantage of formaldehyde is that it does not accumulate in the environment since it is completely oxidized to carbon dioxide within a relatively short time. In the cosmetics industry, formaldehyde is employed as a preservative in hundreds of products, for example, soaps, deodorants, shampoos, and nail – hardening preparations; in some of these items, upper limits have been set for the formaldehyde concentration due to its sensitizing effect (cf. Table 8). Formaldehyde solutions are also used as a preservative for tanning liquors, dispersions, crop protection agents, and wood preservatives. Furthermore, formaldehyde is required in the sugar industry to prevent bacterial growth during syrup recovery.

9. Economic Aspects

Formaldehyde is one of the most important basic chemicals and is required for the manufacture of thousands of industrial and consumer products. It is the most important industrially produced aldehyde.

Formaldehyde can seldom, if ever, be replaced by other products. Substitutes are generally more expensive; moreover, their toxicities have been less thoroughly investigated than that of formaldehyde.

Worldwide capacity [1], [231] is approximately 8.7×10^6 t/a in 1996 (see Table 11; the values are based on 100 % formaldehyde); the five largest manufactures account for ca. 25 % of this capacity:

Borden	0.66×10^6 t / a
BASF	0.444×10^6 t / a
Hoechst Celanese	0.38×10^6 t / a
Georgia Pacific	0.38×10^6 t / a
Neste Resins	0.37×10^6 t / a

Table 11. Worldwide formaldehyde production capacities in 1996 [1], [231]

Country	Total capacity, 10^3 t/a
Western Europe	3119
Germany	1464
Italy	389
Spain	265
United Kingdom	197
France	126
Sweden	124
Netherlands	115
Others	439
Eastern Europe	1850
North America	2008
United States	1772
Canada	236
South America	253
Mexico	65
Chile	63
Brazil	48
Argentina	44
Others	33
Japan	651

The three leading countries with a capacity share of about 45 % are:

United States	1.77×10^6 t/a
Germany	1.46×10^6 t/a
Japan	0.65×10^6 t/a

Formaldehyde consumption is ca. 6×10^6 t/a, although present data about capacity use in Eastern Europe are not available. The demand and the estimated average annual growth rate in the Western hemisphere is summarized in Table 12.

Table 12. Consumption of formaldehyde in the United States, Western Europe, and Japan in 1995 [1], [231]

	United States	Western Europe	Japan
Consumption, 10^6 t/a	1.37	2.22	0.52
Use, %			
Urea – formaldehyde resin	32	50	27
Melamine – formaldehyde resin	4	6	
Phenol – formaldehyde resin	24	10	6
Polyoxymethylenes	10	10	24
1,4-Butanediol	11	7	
MDI	5	6	4
Others	14	11	39
Average annual growth rate, %	2.5	1.5	2.0

Formaldehyde and its associated products are used in ca. 50 different branches of industry, as described in Chapter 8.

In the mid 1980s the sales of industrial products derived from formaldehyde was more than $DM\ 300 \times 10^9$ in the Federal Republic of Germany [132]. At least 3×10^6 people in the Federal Republic of Germany work in factories that use products manufactured from formaldehyde.

10. Toxicology and Occupational Health

Formaldehyde toxicity was investigated extensively during the last decades and comprehensive reviews are available [233–235]. Formaldehyde is an essential intermediate in cellular metabolism in mammals and humans, serving as a precursor for the biosynthesis of amino acids, purines and thymine. Exogenously administered formaldehyde is readily metabolized by oxidation to formic acid or reacts with biomolecules at the sites of first contact. Inhalation exposure of rats, monkeys and humans to irritant concentrations did not increase blood formaldehyde levels, which were found to be around 80 mM (= 2.4 ppm) in these species.

Formaldehyde gas is toxic via inhalation and causes irritation of the eyes and the mucous membranes of the respiratory tract. Concentration – response relationship following human exposure is given in Table 13. Aqueous formaldehyde solutions cause concentration dependent corrosion or irritation and skin sensitization. There is no evidence for Formaldehyde to cause respiratory allergy [236].

Table 13. Dose – response relationship following human exposure to gaseous formaldehyde [133], [134]

Effect	Exposure level, ppm
Odor threshold	0.05 – 1.0
Irritation threshold in eyes, nose, or throat	0.2 – 1.6
Stronger irritation of upper respiratory tract, coughing, lacrimation, extreme discomfort	3 – 6
Immediate dyspnea, burning in nose and throat, heavy coughing and lacrimation	10 – 20
Necrosis of mucous membranes, laryngospasm, pulmonary edema	> 50

In *chronic inhalation* studies with rats, mice, hamsters, and monkeys no systemic toxicity occurred in irritant concentrations. Upper respiratory tract irritation ceased at concentrations < ca. 1 ppm. At concentrations above 1 – 2 ppm changes in the nasal mucosa (respiratory epithelium) occur. At high concentrations (15 – 20 ppm) olfactory epithelium, laryngeal mucosa, and proximal parts of the tracheal epithelium might also be affected. The lesions are characterized by epithelial hyperplasia and metaplasia. Studies using other routes of administration also failed to show systemic toxicity or reproductive effects.

Formaldehyde was *genotoxic* in several in vitro test systems. In animals, there are some indications of in vivo genotoxicity in tissues of initial contact (portal of entry) but not in remote organs or tissues. In workers exposed to formaldehyde no systemic genotoxicity and no convincing evidence of local genotoxicity was found.

No evidence of systemic *carcinogenicity* was found after oral dermal and inhalative administration of formaldehyde. Several chronic inhalation studies in rats showed development of nasal tumors starting at concentrations at or above 6 ppm, causing in addition severe chronic epithelial damage in the nasal epithelium [237]. The nonlinear concentration response curve shows a disproportionately high increase in tumor incidence at concentrations of 10 and 15 ppm. The same nonlinear concentration response was observed for DNA protein cross-link (DPX) formation in nasal mucosa, which is a surrogate of formaldehyde tissue “dose”, and for increase in cell proliferation in nasal epithelium. This leads to the suggestion that increased cell proliferation is a prerequisite for tumor development [237]. Chronic inhalation studies in mice failed to show statistically significant increases in tumor incidences at similar concentrations while in hamsters no nasal tumors were found. This may be attributed to differences in local formaldehyde tissue dose or lower susceptibility of the species for nasal tumor formation.

In humans numerous *epidemiological studies* failed to give convincing evidence of carcinogenicity [235]. IARC [234] concluded that the epidemiologic data available represent “limited evidence of carcinogenicity” and classified formaldehyde as “probably carcinogenic to

humans (Group 2A)". The European Union categorizes the compound as "possibly carcinogenic to humans (Class 3)".

Current occupational exposure limits in different countries vary between 0.3 and 2 ppm [238]. Proposed limit values for indoor air are in the range of 0.1 ppm [239].

11. Low Molecular Mass Polymers

The ability of formaldehyde to react with itself to form polymers depends directly on the reactivity of formaldehyde as a whole. Two different types of formaldehyde polymers are possible and are based on the following structural elements:

1. $-\text{CH}_2-\text{O}-$
2. $-\text{CH}(\text{OH})-$

The polyhydroxyaldehydes consist of the structural unit (2). The highest molecular mass representatives of this group are the sugars. Although these substances can be made by aldol condensation of formaldehyde, they do not revert to formaldehyde on cleavage, and are not discussed in this article.

The representatives of group (1), the real formaldehyde polymers (polyoxymethylenes), revert to formaldehyde on cleavage and, therefore, can be considered as a solid, moisture-free form of formaldehyde. If these linear or cyclic compounds contain no more than eight formal-

dehyde units, they are defined as low molecular mass polymers. The high molecular mass substances are the real polymers (paraformaldehyde, acetal plastics, see also \rightarrow Polyoxymethylenes). Chemical and physical analyses of these low and high molecular mass compounds as well as investigation of their chemical reactions led to the elucidation of the molecular structure of polymers in general [135].

11.1. Linear Polyoxymethylenes

Apart from the poly(oxymethylene) glycols, also called poly(oxymethylene) dihydrates or simply polyoxymethylenes, of the formula $\text{HO}-(\text{CH}_2\text{O})_n-\text{H}$, derivatives such as poly(oxymethylene) diacetates $\text{CH}_3\text{COO}(\text{CH}_2\text{O})_n-\text{COCH}_3$ and poly(oxymethylene) dimethyl ethers $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ should be mentioned. Some of their physical properties are given in Table 14. The n values of the real low molecular mass polyoxymethylenes are 2 – 8; the n values of paraformaldehyde are 8 – 100. However, high polymers with a degree of polymerization n 3000 are also obtained. The polyoxymethylenes are also classified as α , β , γ , δ , and ϵ polymers which are of historical importance. They differ in their degrees of polymerization and in their chemical structures (Table 15). Their toxicology is the same as that of formaldehyde (see Chap. 10).

The lower poly(oxymethylene) glycols are colorless solids with melting points between 80 and 120 °C (Table 14). In contrast to the high

Table 14. Physical properties of low molecular mass poly(oxymethylene) glycols $\text{HO}-(\text{CH}_2\text{O})_n-\text{H}$ and their derivatives

n	Poly(oxymethylene) glycols		Poly(oxymethylene) diacetates			Poly(oxymethylene) dimethyl ethers		
	fp , °C	Solubility in acetone	fp , °C	bp , °C	ρ , g/m ³ (13 Pa, 24 °C)	fp , °C	bp , °C (101.3 kPa)	ρ , g/cm ³ (25 °C)
2			-23	39 – 40	1.128			
3	82 – 85	Very soluble in the cold	-13	60 – 62	1.158	-69.7	105.0	0.9597
4	82 – 85	Very soluble in the cold	-3	84	1.179	-42.5	155.9	1.0242
5	95 – 105 (decomp.)	Very soluble in the cold	7	102 – 104	1.195	-9.8	201.8	1.0671
6			17	124 – 126	1.204	18.3	242.3	1.1003
7		Soluble in the cold	ca. 15	180 – 190				
8		Soluble in the cold	ca. 15	180 – 190				
9	115 – 120 (decomp.)	Soluble when heated	32 – 34		1.216*			

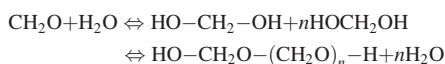
*Value at 13 Pa and 36 °C.

Table 15. Structure and synthesis of $\alpha - \epsilon$ polyoxymethylenes [136]

Polymer	Formula	Synthesis
Paraformaldehyde	HO (CH ₂ O) _n H <i>n</i> = 8 – 100	from aqueous formaldehyde solution [137]
α -Polyoxymethylene	HO (CH ₂ O) _n H <i>n</i> > 100	from aqueous formaldehyde solution [137]
β -Polyoxymethylene	HO (CH ₂ O) _n H <i>n</i> > 200	by heating paraformaldehyde [138]
γ -Polyoxymethylene	H ₃ CO (CH ₂ O) _n CH ₃ <i>n</i> = 300 – 500	from a methanolic paraformaldehyde solution in the presence of sulfuric acid [139]
δ -Polyoxymethylene	H ₃ CO [CH ₂ OC(OH)HO] _n CH ₃ <i>n</i> = 150 – 170	by prolonged boiling of γ -polyoxymethylene with water [138]
ϵ -Polyoxymethylene	HO (CH ₂ O) _n H <i>n</i> > 300	by sublimation of 1,3,5-trioxane [138]

molecular mass materials, they dissolve in acetone and diethyl ether without or with only slight decomposition; they are insoluble in petroleum ether. When dissolved in warm water, they undergo hydrolysis to give a formaldehyde solution. The low molecular mass polymers constitute a homologous series, whose properties change continuously with the degree of polymerization.

A freshly prepared, aqueous formaldehyde solution polymerizes to the lower polymers when allowed to stand (see also Section 2.2). Indeed, formaldehyde exists in dilute solution as dihydroxymethylene (formaldehyde hydrate), which in turn undergoes polycondensation to yield low molecular mass poly(oxymethylene) glycols:



Equilibrium is attained under the influence of a hydrogen ion catalyst. At a low temperature and a high concentration, equilibrium favors formation of high molecular mass polymers. However, the major product is of lower molecular mass when the system is heated. The polymers partially separate out, crystallize, and slowly undergo further condensation polymerization [140]. The low molecular mass substances can be further precipitated and isolated by concentrating the solution at low temperature under vacuum conditions; the polymers can be further precipitated by evaporation [141]. The resulting mixture can be separated into the individual substances by exploiting their varying solubilities in different solvents [135].

The transformation of poly(oxymethylene) dihydrates to diacetates and, above all, to diethers

produces a remarkable increase in thermal and chemical stability. This is because the unstable hemiacetals at the ends of the chains are eliminated through saturation of the hydroxyl groups. The diethers are stable up to 270 °C in the absence of oxygen and up to 160 °C in the presence of oxygen. These diethers and diacetates are resistant to hydrolysis under neutral conditions, the diethers are also stable in the presence of alkali. Similar to the dihydrates, the properties of the diacetates and diethers also change continuously as the degree of polymerization increases (see Table 14).

Poly(oxymethylene) diacetates are produced by the reaction of paraformaldehyde with acetic anhydride [135]. Pure products are isolated by vacuum distillation, solvent extraction, and crystallization.

The formation of poly(oxymethylene) dimethyl ethers involves the reaction of poly(oxymethylene) glycols or paraformaldehyde with methanol at 150 – 180 °C in the presence of traces of sulfuric or hydrochloric acid in a closed vessel [135]. Alternatively, they can be synthesized by the reaction of formaldehyde dimethyl acetal with either paraformaldehyde or a concentrated formaldehyde solution in the presence of sulfuric acid. This synthesis can be varied by substituting other formaldehyde dialkyl acetals for the dimethyl compound [142].

Paraformaldehyde. [30525-89-4] was first produced in 1859. This polymer, at first mistakenly called dioxymethylene and trioxymethylene, consists of a mixture of poly(oxymethylene) glycols HO-(CH₂O)_n-H with *n* = 8 – 100. The formaldehyde content varies

Table 16. Vapor pressure of formaldehyde (p) released from paraformaldehyde

$t, ^\circ\text{C}$	10	21	25	33	37
p, kPa	0.112	0.165	0.193	0.408	0.667
$t, ^\circ\text{C}$	43	47	51	58	65
p, kPa	0.943	1.096	1.376	1.808	20.8
$t, ^\circ\text{C}$	80	90	100	110	120
p, kPa	32.8	44.1	49.6	53.5	78.3

*Values up to 58 °C according to [143] and from 65 – 120 °C according to [144].

between 90 and 99 % depending on the degree of polymerization n (the remainder is bound or free water). It is an industrially important linear polyoxymethylene.

Properties. Paraformaldehyde is a colorless, crystalline solid with the odor of monomeric formaldehyde. It has the following physical properties: fp 120 – 170 °C, depending on the degree of polymerization; heat of combustion 16.750 kJ/kg (product containing 98 wt % formaldehyde); energy of formation 177 kJ/mol formaldehyde (product containing 93 wt % formaldehyde); flash point 71 °C; ignition temperature of dust 370 – 410 °C; lower explosion limit of dust 40 g/m³ (the last three values strongly depend on the particle size); minimum ignition energy 0.02 J.

Even at ambient temperature, paraformaldehyde slowly decomposes to gaseous formaldehyde (Table 16), a process which is greatly accelerated by heating. Depolymerization is based on a chain “unzipping” reaction which starts at the hemiacetal end groups of the individual molecules. The rate of decomposition therefore depends on the number of end groups, i.e., on the degree of polymerization.

Paraformaldehyde contains only a few acetone-soluble components (lower diglycols). It dissolves slowly in cold water, but readily in warm water where it undergoes hydrolysis and depolymerization to give a formaldehyde solution. Although this solution is generally cloudy as a result of impurities, these can be removed by filtration. Indeed, the resulting solution is identical with the solution obtained on dissolving gaseous formaldehyde in water. Not only heat, but also dilute alkali or acid increase the solubility of paraformaldehyde. Alkali catalyzes formaldehyde cleavage at the chain ends, acid causes

additional splitting at the oxygen bridges. The rate constant of dissolution passes through a minimum between pH 2 and 5, it increases rapidly above and below this pH range [145]. The situation becomes more complex at higher concentrations of formaldehyde in the solution due to the incipient back reaction. Solubility in non-aqueous solvents is also improved in the presence of acidic or alkaline agents as a result of the onset of depolymerization. Paraformaldehyde also dissolves in alcohols, phenols, and other polar solvents, in which depolymerization and solvation can occur.

Production. Paraformaldehyde is prepared industrially in continuously operated plants by concentrating aqueous formaldehyde solutions under vacuum conditions. At first, colloidal, waxy gels are obtained, which later become brittle. The use of a fractionating column through which gases were passed dates from about 1925 [146], [147].

Paraformaldehyde is currently produced in several steps which are carried out at low pressure and various temperatures [148], [149]. Highly reactive formaldehyde is produced under vacuum conditions starting with solutions that contain 50 – 100 ppm of formic acid and also 1 – 15 ppm of metal formates where the metals have an atomic number of 23 – 30 (e.g., Mn, Co, and Cu) [150]. The solutions are processed in thin-layer evaporators [151] and spray dryers [152].

Other techniques such as fractional condensation of the reaction gases in combination with the formaldehyde synthesis process [153] and very rapid cooling of the gases [154] are also applied. Alternatively, formaldehyde-containing gas is brought into contact with paraformaldehyde at a temperature that is above the dew point of the gas and below the decomposition temperature of paraformaldehyde [155]. The product is obtained in the form of flakes when a highly concentrated formaldehyde solution is poured onto a heated metal surface. The hardened product is subsequently scraped off and thoroughly dried [156]. Paraformaldehyde beads are produced by introducing a highly concentrated melt into a cooling liquid (e.g., benzene, toluene, cyclohexane [157]). Acids [158] and alkalis [148], [159] are also added; they apparently accelerate polymerization and lead to the forma-

tion of higher molecular mass but less reactive paraformaldehyde.

Highly soluble, highly reactive paraformaldehyde with a low degree of polymerization is very much in demand. It is produced from concentrated, aqueous – alcoholic formaldehyde solutions [160], [161].

Stabilizing agents include hydantoins [162], nicotinamide, and succinamide [163].

Producers. The main producers of paraformaldehyde are Degussa (Federal Republic of Germany), Ticona (owned by Hoechst, United States), Mitsui Toatsu, and Mitsubishi Gas (Japan). Smaller producers include Derivados Forestales (Spain), Synthite (United Kingdom), Alder (Italy), and Lee Chang Yung (Taiwan).

Quality Specifications. An important factor regarding the quality of paraformaldehyde is its tendency to “age”, especially under the influence of heat, which results in decreased reactivity. The paraformaldehyde loses its residual water and becomes brittle. This may be prevented by storage below 10 °C; in a moist atmosphere regeneration is possible. After production, the residual moisture in the product should therefore be retained.

Reactivity is determined with the aid of the resorcinol test in which the rate at which paraformaldehyde condenses with resorcinol in an alkaline medium is measured [162]. The formaldehyde content is measured by using the sodium sulfite method (cf. Section 6.2) and the water content by the Karl Fischer method.

Transport and Storage. Paraformaldehyde is stored and transported as granules or a free-flowing coarse powder in bags, containers, and in silos or silo wagons. Cool, dry conditions must be maintained.

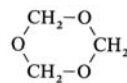
Uses. Paraformaldehyde is used in place of aqueous formaldehyde solutions, especially in applications where the presence of water interferes, e.g., in the plastics industry for the preparation of phenol, urea, and melamine resins, varnish resins, thermosets, and foundry resins. Other uses include the synthesis of organic products in the chemical and pharmaceutical industries (e.g., Prins reaction, chloromethylation, Mannich reaction), the production of textile aux-

iliaries (e.g., for crease-resistant finishes), and the preparation of disinfectants and deodorants.

11.2. Cyclic Polyoxymethylenes

11.2.1. Trioxane

1,3,5-Trioxane [110-88-3], trioxymethylene, or 1,3,5-trioxycyclohexane, $C_3H_6O_3$, M_r 90.1, is the cyclic trimer of formaldehyde and was first produced and identified in 1885. A laboratory oddity for many years, this substance is very important today, especially as an intermediate in the production of acetal resins (polyoxymethylenes).



Physical Properties. Trioxane is a white crystalline solid with a characteristic odor resembling that of chloroform. Other physical properties are as follows (see also [164]):

<i>f</i> _p	62 – 63 °C
<i>b</i> _p	115 °C
Density of crystals	1.39 kg/m ³
Density of liquid at 65 °C	1.17 kg/m ³
Refractive index n_D^{20} at 65 °C	1.3891
Specific heat	1.23 kJ kg ⁻¹ K ⁻¹
Heat of fusion	222 kJ/kg
Heat of evaporation	452 kJ/kg
Trouton constant	25
Heat of formation	180 kJ/mol formaldehyde
Heat of combustion	16.850 kJ/kg

Vapor pressure

<i>t</i> , °C	25	37.5	86	87	90	114.5	129
<i>p</i> , kPa	1.69	4.16	37.7	39.5	44.0	101.2	161.8

Flash point	45 °C
Ignition temperature	410 °C
Lower explosion limit (38 °C)	3.57 vol %
Upper explosion limit (75 °C)	28.7 vol %
Dynamic viscosity η	
at 65 °C	2.05 mPa s
at 85 °C	0.91 mPa s

(Continued)

Dielectric constant	
at 20 °C	3.2 – 3.4
at 70 °C	8
Conductance at 78 °C	<1 μ S

For the spectroscopic analytical identification of trioxane, see [164]. The compound forms an azeotropic mixture with 30 wt% water, *bp* 91.3 °C.

Trioxane is soluble in water (0.172 g/cm³ at 18 °C, 0.211 g/cm³ at 25 °C and completely soluble at 100 °C), alcohol, ketones, organic acids, ethers, esters, phenols, aromatic hydrocarbons, and in chlorinated hydrocarbons; however, it is only sparingly soluble in aliphatic hydrocarbons.

Like dioxane and other cyclic ethers, melted trioxane, (mixed with water if necessary) is an excellent solvent for organic substances. It forms addition compounds with phenol and 1,3,5-trinitrobenzene.

Studies of vapor-liquid equilibria of systems containing formaldehyde, water, methanol, and trioxane are available [220], [224], [226].

Chemical Properties. Trioxane is stable up to 224 °C. Like acetals, it is hydrolyzed by aqueous solutions of strong acids. However, trioxane is inert under neutral and alkaline conditions. For this reason, the usual detection methods for formaldehyde, such as the sodium sulfite method, cannot be applied directly. Formaldehyde in acetals, and thus trioxane, can be determined by heating in water in the presence of a

strong acid (e.g., sulfuric acid) to convert the product to monomeric formaldehyde. The formaldehyde can then be determined by the sulfite method (see Section 6.2).

The acid-catalyzed hydrolysis of trioxane is accelerated by using stronger acids, higher acid concentrations, and nonaqueous solvents. When trioxane is heated in nonaqueous systems in the presence of either strong acids (sulfuric acid, hydrochloric acid, zinc chloride, iron chloride etc.) or comonomers, it is converted to high molecular mass oxymethylene homopolymers or oxymethylene copolymers, respectively. This method is applied today in the large-scale production of acetal resins. If additional substances which react with formaldehyde (e.g., phenols, melamine) are also present during these hydrolytic or moisture-free reactions, then the nascent formaldehyde reacts very vigorously with them.

Production. Trioxane is prepared by the trimerization of formaldehyde. At first, the starting materials used were paraformaldehyde or polyoxymethylenes which were heated with acid, usually sulfuric acid [165]. As the commercial importance of trioxane grew, aqueous formaldehyde solutions and high formaldehyde concentrations [166] were introduced. World production in 1987 was 250 000 t, in 1997 about 380 000 t.

The currently preferred process for trioxane production is illustrated in Figure 5 (see also

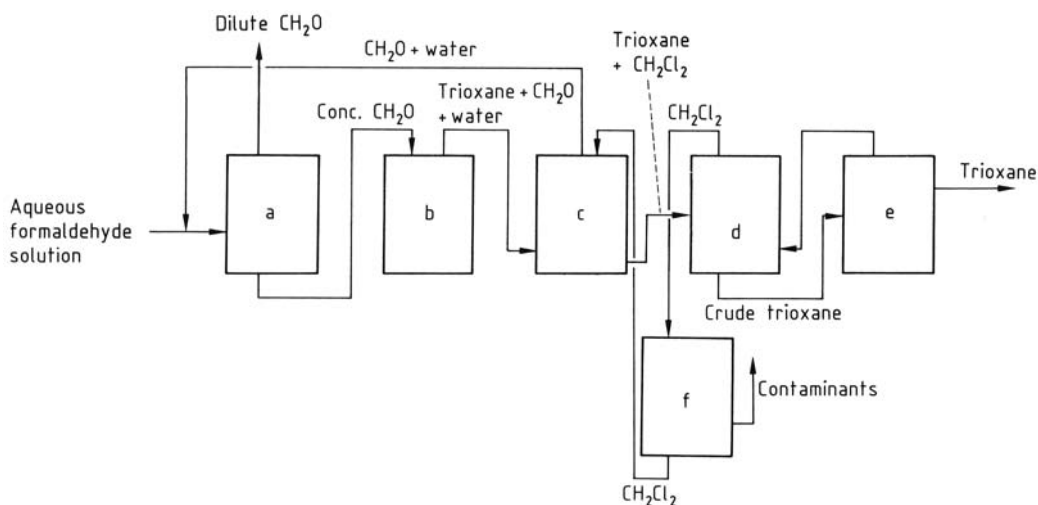


Figure 5. Trioxane production

a) Concentration column; b) Reactor; c) Extraction column; d, e) Distillation columns; f) Solvent purification

[167]). Commercial aqueous formaldehyde is concentrated to 60 – 65 wt% in a column (a) under vacuum conditions. The 60 – 65 % formaldehyde solution is fed into the reactor (b). A dilute (6 – 10 %) formaldehyde solution is removed and, if necessary, can be reconcentrated by pressure distillation and returned to the process. In the reactor (b), formaldehyde is trimerized in the presence of a catalyst (e.g., sulfuric acid, phosphoric acid, ion exchanger [168], or heteropoly acid [169]) which is present at a concentration of up to 25 wt% [170]. Technical and kinetic experiments designed to achieve optimal reactor conditions are described in [171]. A mixture of trioxane, formaldehyde, and water is distilled off and, if necessary, concentrated in a distillation column [172]. In the extraction column (c) [173], the trioxane is extracted from the aqueous mixture by using methylene dichloride [75-09-2] [166] or another inert, water-immiscible solvent (benzene [174], 1,2-dichloroethane [175], or nitrobenzene [176]). The formaldehyde – water mixture is returned to the concentrating column (a). The trioxane – methylene dichloride mixture is separated in the distillation column (d). The crude trioxane is obtained at the bottom of the column and the methylene dichloride as overhead product. The trioxane is subsequently purified by distillation in column (e). The solvent methylene dichloride is freed of impurities in the solvent purification step (f) and recycled to the extraction column (c).

Impurities and byproducts (formic acid, methyl formate, dimethylformal, and formaldehyde) can be eliminated by washing with sodium hydroxide solution after the extraction step [177]. Emulsification of the reaction mixture in an inert, nonvolatile liquid, e.g., paraffin oil, may reduce the formation of paraformaldehyde in the reactor [178]. Addition of inert organic substances with low dielectric constants to the trimerization mixture increases conversion [179]. Special processes in a synthesis reactor have also been described [180]. Crystallization of liquid trioxane and contact with an inert gas stream can be used for further purification, especially from higher homologues of bis (methoxymethyl) ether [181].

In the last years a new method has been proposed to remove trioxane from the mixture of trioxane, formaldehyde, and water. After trimerization formaldehyde is separated by perva-

poration, e.g., with a polyether block amide membrane [182], [183].

Since water is added with the aqueous formaldehyde solution, the energy requirement for trioxane production is very high (14 – 17 t of steam per ton of trioxane). This may be reduced by using a process based on the trimerization of gaseous formaldehyde with Lewis acids [184] and catalyzed by vanado- and/or molybdo and/or wolframo-phosphoric acids [185–187].

Trioxane can be produced by recycling of polyoxymethylenes (POM) [188], [189].

Producers. Ticona (owned by Hoechst, Federal Republic of Germany and United States), Ultraform (owned by BASF and Degussa, Federal Republic of Germany and United States), Polyplastics (owned by Hoechst and Daicel, Japan), Mitsubishi Gas Chemical (Japan), Asahi (Japan), Korean Engineering Plastics (owned by Tong Yang Nylon and Mitsubishi Gas Chemical, Korea), Taiwan Engineering Plastics, Tepco (owned by Polyplastics and Chang Chun Group, Taiwan), Formosa Plastics (Taiwan), Tarnoform (Poland). The world capacity is about 400 000 t.

Uses. The production of plastics (polyoxymethylene plastics, POM) is the most important commercial application of trioxane and requires extremely pure material. Since trioxane depolymerizes to produce formaldehyde, it can be used in almost all formaldehyde reactions, especially when anhydrous formaldehyde is desired. Trioxane is used, e.g., as a textile auxiliary; in various cross-linking agents, for instance for pitch fibers in manufacturing of carbon fibers; for stabilization and reinforcement of wood to produce musical instruments; and in distillable binders in ceramic compositions for shaped articles, e.g., in an injection moulding process. It is also employed in the stabilization and deodorization of waxes, as an anticorrosive additive for metals (especially when corrosion is caused by chlorinated hydrocarbons) [190], as an additive in photographic developers, as a solid fuel, in coating removers and, because of its hydrolysis to formaldehyde in presence of acid, in disinfectants.

Storage and Transport. Liquid trioxane is stored and transported in heated tanks. Solid

trioxane is transported in drums, trioxane flakes are transported in drums and bags.

Toxicology. Trioxane is not known to display any special toxic reactions; its oral LD₅₀ value in rats is > 3200 mg/kg. Hydrolysis in the presence of acid produces formaldehyde (see Chap. 10).

11.2.2. Tetraoxane

1,3,5,7-Tetraoxane [293-30-1], tetraoxymethylene, or 1,3,5,7-tetroxocane, C₄H₈O₄, *M_r* 120, is the cyclic tetramer of formaldehyde and is a crystalline solid (*fp* 112 °C). Tetraoxane vapors are stable even at 200 °C (*bp* at 101.3 kPa, 163 – 165 °C).

Tetraoxane is produced by heating a water-insoluble, high molecular mass poly(oxymethylene) diacetate [165]. In the tetramerization of formaldehyde, metal sulfates may be used as catalyst [191].

Tetraoxane accumulates as a high-boiling substance in the distillation residue obtained during the production of trioxane. It is also obtained in the polymerization of trioxane and can be isolated by extraction with, for example, ethylbenzene [192]. The formation of tetraoxane by irradiation of carbon monoxide and hydrogen has also been described [193].

Tetraoxane is a more favorable textile auxiliary for achieving crease resistance, e.g., for cellulose fibers, than trioxane because of its higher boiling point. Like trioxane, tetraoxane can also be employed in the production of acetal plastics.

11.2.3. Higher Cyclic Polyoxymethylenes

Higher cyclic polyoxymethylenes can also undergo polymerization. The tendency to polymerize in the melt decreases with increasing ring size.

1,3,5,7,9-Pentoxecane [16528-92-0], penta-oxane, penta-oxacyclodecane, or penta-oxymethylene, C₅H₁₀O₅, the cyclic pentamer of formaldehyde, is a crystalline product (*fp* 55 – 56 °C). The polymerization of trioxane with the aid of a tin tetrachloride catalyst pro-

duces several cyclic homologues including pentoxecane [194].

The fractional distillation and subsequent comparative gas chromatography of residues from the commercial trioxane polymerization affords 1,3,5,7,9-pentoxecane [195].

Although *hexoxecane* (six formaldehyde units) has not clearly been identified in the residue, *Pentadecoxane* (15 formaldehyde units) has been unambiguously detected (*fp* 68 – 70 °C). Pentoxecane is used in addition to tetraoxane in patent formulations for the shrinkproofing of cotton [196].

12. Formaldehyde Cyanohydrin

Formaldehyde cyanohydrin [107-16-4], CH₂(OH)CN, *M_r* 57.05, is also known as hydroxyacetone nitrile, glycolonitrile, or glycolic nitrile. It is less commercially important than acetone cyanohydrin (→ Acetone) but of about the same importance as the cyanohydrin derivatives of acetaldehyde, benzaldehyde, and ethylene.

Physical Properties. Formaldehyde cyanohydrin is a colorless liquid with an odor similar to that of hydrogen cyanide. It is soluble in water, ethanol, and diethyl ether but insoluble in chloroform and benzene. For IR spectrum see [197]. Other physical properties follow:

<i>mp</i>	–72 °C
<i>bp</i> at	
101.3 kPa	183 °C (slight decomp.)
3.2 kPa	119 °C
0.4 kPa	76.5 – 78 °C
Relative density <i>d</i> ₄ ⁹	1.1039
<i>n</i> _D ²⁰	1.4112
Electrolytic dissociation constant <i>k</i> at 25 °C	0.843 × 10 ^{–5}
Dielectric constant	178

Chemical Properties. Like all cyanohydrins, reactions can occur at both the nitrile and the hydroxyl groups of formaldehyde cyanohydrin. Heating at 100 °C with water yields hydroxyacetamide, acid-catalyzed hydrolysis yields hydroxyacetic acid. Reaction with absolute ethanol in the presence of hydrochloric acid produces ethyl hydroxyacetate [198]. *N*-Substituted

amides can be synthesized by heating formaldehyde cyanohydrin with amines in water [199]. Catalytic hydration (Ni – Al catalysts) of the nitrile group gives amines. The resulting mixtures can be separated into primary, secondary, and tertiary β -hydroxyethyleneamines [200].

The hydroxyl group of formaldehyde cyanohydrin can be replaced by other electronegative groups. For example, reaction with ammonia gives amino nitriles including nitrilotriacetone nitrile $N(\text{CH}_2\text{CN})_3$, which is an intermediate in the synthesis of nitrilotriacetic acid (NTA) [201]. Ethylenediaminetetraacetone nitrile is similarly synthesized from formaldehyde cyanohydrin and ethylene diamine in the presence of sulfuric acid as a catalyst. Subsequent hydrolysis yields ethylenediaminetetraacetic acid (EDTA) [201]. The reaction of cyanohydrins with ammonia is a step in the Strecker synthesis of amino acids. Hydration of formaldehyde cyanohydrin and subsequent treatment with an aqueous solution of sodium cyanide and ammonia (Bucherer reaction, a variant of the Strecker synthesis) leads to *DL*-serine [202].

Formaldehyde cyanohydrin reacts with hydrogen halides or phosphorus pentachloride to form α -halonitriles. In aqueous solutions at pH 8 and a temperature of 10 °C or less, it trimerizes to form 4-amino-2,5-bis(hydroxymethyl)-pyrimidin-5-ol [203]. Hydantoin can be synthesized by reacting formaldehyde cyanohydrin with carbon dioxide, ammonia, or ammonium carbonate at high pressure [204], [205].

Production. Formaldehyde cyanohydrin is formed in 79.5 % yield when 37 % formaldehyde is mixed with a stoichiometric amount of aqueous hydrogen cyanide for 1 h at 2 °C in the presence of sodium hydroxide as a catalyst [206]. Patents also describe synthesis by (1) heating formaldehyde with hydrogen cyanide at 250 °C [207] or in the presence of sulfur dioxide at pH 1.5 – 2.0 in an aqueous medium [208] and (2) by reacting acetonitrile with oxygen and with or without water at high pressure in the presence of various vanadium oxides [209–211].

Formaldehyde cyanohydrin is generally handled as an aqueous solution but it can also be isolated in the anhydrous state by ether extraction, drying, and vacuum distillation [212]. Although the extremely pure product is reported to be very stable [213], addition of a small amount

of stabilizer (e.g., monochloroacetic, mercaptoacetic, lactic, sulfonic, and phosphoric acids) is advisable [214]. Monochloroacetic acid is especially suitable because it codistills with the product. Cyanohydrin with a lower degree of purity is not very stable, especially at high pH values, this should be borne in mind when handling anhydrous formaldehyde cyanohydrin (see also [203]).

Transport and Storage. Formaldehyde cyanohydrin is used almost exclusively as an intermediate and is normally produced at the site where it is to be processed. However, it is also supplied as a 70 % aqueous solution and is transported in steel containers and tank cars. Attention should be paid to stabilization during transport and storage. Impure formaldehyde cyanohydrin can decompose to give formaldehyde and hydrogen cyanide, attention should therefore be paid to explosion and fire hazards.

Toxicology. Formaldehyde cyanohydrin, like all cyanohydrins, is extremely toxic when inhaled or ingested and moderately toxic when absorbed via the skin [215]. All forms of contact should be avoided because of the possible formation of hydrogen cyanide or cyanides.

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