1. Introduction

Acetaldehyde (ethanal), CH$_3$CHO [75-07-0], was observed in 1774 by Scheele during reaction of black manganese dioxide and sulfuric acid with alcohol. Its constitution was explained in 1835 by Liebig who prepared pure acetaldehyde by oxidation of ethanol with chromic acid and designated this product “aldehyde,” a contraction of the term “alcohol dehydrogenatus.”

Acetaldehyde is a mobile, low-boiling, highly flammable liquid with a pungent odor. Because of its high chemical reactivity, acetaldehyde is an important intermediate in the production of acetic acid, acetic anhydride, ethyl acetate, peracetic acid, butanol, 2-ethylhexanol, pentaerythritol, chlorinated acetaldehydes (chloral), glyoxal, alkyl amines, pyridines, and other chemicals. The first commercial application was the production of acetone via acetic acid between 1914 and 1918 in Germany (Wacker-Chemie and Hoechst) and in Canada (Shawinigan).

Acetaldehyde is an intermediate in the metabolism of plant and animal organisms, in which it can be detected in small amounts. Larger amounts of acetaldehyde interfere with biological processes. As an intermediate in alcoholic fermentation processes it is present in small amounts in all alcoholic beverages, such as beer, wine, and spirits. Acetaldehyde also has been detected in plant juices and essential oils, roasted coffee, and tobacco smoke.

Commercial production processes include dehydrogenation or oxidation of ethanol, addition of water to acetylene, partial oxidation of hydrocarbons, and direct oxidation of ethylene. In the 1970s, the world capacity of this last process, the Wacker-Hoechst direct oxidation, increased to over 2×10$^6$ t/a. However, the importance of acetaldehyde as an organic
intermediate is now steadily decreasing, because new processes for some acetaldehyde derivatives have been developed, such as the oxo process for butanol and 2-ethylhexanol and the Monsanto process for acetic acid. In the future, new processes for acetic anhydride (Halcon, Eastman, Hoechst), for vinyl acetate (Halcon), and for alkyl amines (from ethanol) will diminish the use of acetaldehyde as a starting material.

2. Physical Properties

Acetaldehyde, C₃H₄O, Mᵣ 44.054, is a colorless liquid with a pungent, suffocating odor that is slightly fruity when diluted.

### Table 1: Physical Properties of Acetaldehyde

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>bp (kPa) at 101.3°C</td>
<td>20.16 °C</td>
</tr>
<tr>
<td>mp (°C)</td>
<td>-123.5 °C</td>
</tr>
<tr>
<td>Critical temperature Tₛ (°C)</td>
<td>181.5 °C</td>
</tr>
<tr>
<td>Critical pressure pₛ (MPa)</td>
<td>6.44 MPa</td>
</tr>
<tr>
<td>Relative density dₛ (g/L)</td>
<td>0.8045 – 0.001325 r</td>
</tr>
<tr>
<td>Refractive index nₛ (r)</td>
<td>1.34240 – 0.0005635 r</td>
</tr>
<tr>
<td>Molar volume of the gas</td>
<td>23.40 L/mol</td>
</tr>
<tr>
<td>Molar volume of the vapor at 20.16°C</td>
<td>23.40 L/mol</td>
</tr>
<tr>
<td>Specific volume of the vapor at 20.16°C</td>
<td>0.531 m³/kg</td>
</tr>
<tr>
<td>Vapor density (air = 1)</td>
<td>1.52</td>
</tr>
</tbody>
</table>

### Other Physical Data

**Viscosity of liquid**
- at 9.5 °C: 0.253 mPa·s
- at 20 °C: 0.21 mPa·s

**Viscosity of vapor**
- at 25 °C: 86 x 10⁻⁴ mPa·s

**Surface tension**
- at 20 °C: 21.2 x 10⁻² mN m⁻¹

**Dipole moment (gas phase)**
- 2.69 ± 2 % D

**Dielectric constant**
- of liquid at 20 °C: 21.8
- of vapor at 20.16 °C, 101.3 kPa: 1.0216

**Heat capacity of liquid**
- C_p (γ) at 0 °C: 2.18 J g⁻¹ K⁻¹
- at 20 °C: 1.38 J g⁻¹ K⁻¹

**Heat capacity of vapor**
- C_p (g) at 25 °C, 101.3 kPa: 1.24 J g⁻¹ K⁻¹

**Critical temperature**
- T_c: 21.8 K

**Critical pressure**
- P_c: 8045 Pa

**Dielectric constant**
- at 20 °C: 1.0216

**Gibbs free energy of formation**
- at 25 °C: -133.81 kJ/mol

**Gibbs free energy of formation for gaseous acetaldehyde**
- at 25 °C: -166.47 kJ/mol

**Latent heat of formation**
- at 25 °C: 265.9 J mol⁻¹ K⁻¹

**Latent heat of vaporization**
- at 20.2 °C: 25.73 kJ/mol

**Latent heat of vaporization for gaseous acetaldehyde**
- at 20.2 °C: 166.4 kJ/mol

**Molecular weight**
- Mᵣ: 44.054

**Molality**
- at 20 °C: 0.1 m

**Moles per liter**
- at 20 °C: 0.2 L mol⁻¹

**Moles per liter at 0 °C**
- 1166.4 kJ/mol

**Moles per liter at 20 °C**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 25 °C**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 298 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 300 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 310 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 320 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 330 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 340 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 350 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 360 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 370 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 380 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 390 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 400 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 410 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 420 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 430 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 440 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 450 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 460 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 470 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 480 K**
- 265.9 J mol⁻¹ K⁻¹

**Moles per liter at 490 K**
- 265.9 J mol⁻¹ K⁻¹
in [25]. For solubility of carbon dioxide, acetylene, and nitrogen in acetaldehyde, see [11]; for freezing points of aqueous acetaldehyde solutions, see [11]; for vapor – liquid equilibria of binary systems of acetaldehyde with water, ethanol, acetic acid, and ethylene oxide, see [26], pp. 392, 561, 565, and 570, with vinyl acetate, see [27].

Safety Data. Flash point (Abel – Pensky; DIN 51 755; ASTM 56 – 70) −20 °C (−40 °C according to the safety regulations of the Berufsgenossenschaft der Chemischen Industrie, Federal Republic of Germany). Ignition temperature (DIN 51 794; ASTM D 2155 – 66) 140 °C; for ignition retardation when injected into a hot air stream, see [28]. Explosive limits in air: 4 – 57 vol %; for influence of pressure on explosive limits, see [29].

3. Chemical Properties and Uses

Acetaldehyde is a highly reactive compound showing all of the typical aldehyde reactions as well as those of an alkyl group in which hydrogen atoms are activated by the carbonyl group in the α position. When heated above 420 °C acetaldehyde decomposes into methane and carbon monoxide.

3.1. Addition Reactions

With water, acetaldehyde forms an unstable hydrate; isolable solid hydrates are known only with chlorinated acetaldehydes. Alcohols add to acetaldehyde giving hemiacetals, which form acetals (→ Aldehydes, Aliphatic) with additional alcohol in the presence of acids by removal of water. Diols give cyclic acetals; for example, 2-methyl-1,3-dioxolane is obtained from ethylene glycol and acetaldehyde, and 2-methyl-1,3-dioxane from 1,3-propanediol.

Aqueous sodium bisulfite solution and acetaldehyde give a crystalline adduct from which acetaldehyde can be liberated. Dry ammonia forms crystalline acetaldehyde ammonia. Acetaldehyde and hydrocyanic acid react to give laconitrile (α-hydroxypropionitrile), a possible intermediate in acrylonitrile production [30].

Acetaldehyde reacts with acetic anhydride to give ethylidene diacetate, an intermediate in the vinyl acetate process of Celanese Corp. [31] (→ Vinyl Esters).

3.2. Derivatives of Aldol Addition

Two molecules of acetaldehyde combine in the presence of alkaline catalysts or dilute acids at room temperature or with moderate heating to form acetaldol [107-89-1], CH₂CH(OH) CH₂CHO. At increased temperatures, water is cleaved easily from this acetaldol, forming crotonaldehyde (→ Aldehydes, Aliphatic). Further condensation under more stringent conditions to form aldehyde resins (e.g., synthetic shellac) now has no industrial importance.

Urea and acetaldehyde condense in the presence of H₂SO₄ to form crotonylidenediurea (6-methyl-4-ureidohexahydropyrimidin-2-one [1129-42-6]), which is used as a long-term nitrogen fertilizer (→ Fertilizers, 1. General).

Acetaldehyde is also an intermediate in the butadiene synthesis starting from acetylene and proceeding via acetaldol and its hydrogenation product, 1,3-butanediol [32]. This process was introduced around 1918 and is still carried out on a commercial scale in some Eastern European countries.

Acrolein is obtained by aldol condensation of acetaldehyde and formaldehyde and subsequent water elimination, analogous to the formation of crotonaldehyde. This method is also without commercial importance today, whereas the production of pentaerythritol from acetaldehyde and a fourfold amount of formaldehyde in the presence of Ca(OH)₂ or NaOH is very important industrially (→ Alcohols, Polyhydric).

3.3. Reaction with Nitrogen Compounds

With primary amines, Schiff bases, CH₃CH=NR, are formed. Nitrogen compounds such as hydroxylamine, hydrazine, phenylhydrazine, and semicarbazide react with acetaldehyde to give easily crystallizable compounds that are used for the analytical determination and characterization of aldehydes (semicarbazone, mp 162 – 163 °C; p-nitrophenylhydrazone, mp
128.5 °C; 2,4-dinitrophenylhydrazone, mp 168 °C; oxime, mp 47 °C). Many other aldehydes and ketones can be characterized in the same way because their analogous derivatives generally have sharp melting points.

The synthesis of pyridine and pyridine derivatives is of increasing importance. 5-Ethyl-2-methylpyridine is obtained in the presence of fluoride ions by the reaction of aqueous ammonia with acetaldehyde (or with paraldehyde, which slowly releases the monomer). In the added presence of formaldehyde or acrolein, mixtures of pyridine and alkylpyridines form (→ Pyridine and Pyridine Derivatives).

3.4. Oxidation

The major part of the acetaldehyde produced commercially is used for manufacturing acetic acid by oxidation with oxygen or air (→ Acetic Acid). Acetaldehyde monoperacetate is formed as an intermediate and decomposes into peracetic acid and acetaldehyde at elevated temperatures and in the presence of catalytic amounts of iron or cobalt salts. In the presence of Mn²⁺ salts, acetic acid is obtained from acetaldehyde monoperacetate, and in the presence of Co²⁺ and Cu²⁺ salts, acetic anhydride can be formed.

Oxidation with nitric acid gives glyoxal (→ Glyoxal and → Glyoxylic Acid). Halogenated acetaldehydes are prepared by halogenation.

Mono-, di-, and trichloroacetaldehydes (→ Chlороacetaldehydes) and tribromoacetaldehyde (bromal) are useful for producing insecticides (e.g., DDT, DDD), pharmaceuticals, and dyes.

3.5. Reduction

Acetaldehyde is hydrogenated readily to ethanol. Prior to 1939, that is, before petrochemically produced ethylene became available in Europe, this reaction was used industrially to produce ethanol from acetaldehyde and, therefore, from acetylene.

Mono-, di-, and triethylamine [75-04-7], [109-89-7], [121-44-8] can be produced from acetaldehyde, ammonia, and hydrogen in the presence of a hydrogenation catalyst [33] (→ Amines, Aliphatic).

3.6. Miscellaneous Reactions

The Tishchenko reaction of acetaldehyde gives the commercially important solvent ethyl acetate (→ Acetic Acid); it is catalyzed by aluminum alcoholate.

As a “radical trapping agent,” acetaldehyde is used to control chain length in the polymerization of vinyl compounds.

Oligomers of acetaldehyde are treated in Chapter 8.

3.7. Consumption

The consumption of acetaldehyde has changed during the last few years. Since 1993 in the USA, acetaldehyde is no longer used for the production of acetic acid, butanol, or 2-ethylhexanol, which are now produced by other routes (Table 1). The consumption of acetaldehyde for some other chemicals like peracetic acid or pyridine bases is increasing.

4. Production

Raw materials that have been used for the production of acetaldehyde are:

<table>
<thead>
<tr>
<th>Table 1. Consumption of acetaldehyde (10³ t) in 2003 [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
</tr>
<tr>
<td>Acetic acid/acetic anhydride</td>
</tr>
<tr>
<td>Acetate esters</td>
</tr>
<tr>
<td>Pentacetyltrithitol</td>
</tr>
<tr>
<td>Pyridine and pyridine bases</td>
</tr>
<tr>
<td>Peracetic acid</td>
</tr>
<tr>
<td>1,3-Butylene glycol</td>
</tr>
<tr>
<td>Others</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

* Included in others (glyoxal/glyoxalic acid, crotonaldehyde, lactic acid, n-butanol, 2-ethylhexanol).
1. Ethanol from fermentation of carbohydrates or from hydration of ethylene
2. Acetylene
3. Ethylene
4. Lower hydrocarbons
5. Carbon monoxide and hydrogen
6. Methanol

The economy of the commercial processes depends essentially upon prices and the availability of raw materials. In highly industrialized countries maintaining high prices for ethanol by fiscal measures or where petrochemical ethanol was not available, as in Germany or Japan before 1939, acetylene was the favored starting material for acetaldehyde. The acetylene process is still operated in some Eastern European countries and also by companies where cheap acetylene is available. Petrochemically produced ethanol, however, was the favored raw material in the other countries, whereas ethanol made by fermentation was and still is used on a small scale in countries with less chemical industry.

In Western countries, including Japan, all these processes have now been almost completely replaced by the direct oxidation process developed in the late 1950s by Wacker-Chemie and Hoechst. This is because ethylene is available at a lower price than acetylene.

Even the two-stage processes using ethanol from ethylene as starting material are no longer competitive because of the decreasing importance of acetaldehyde as an organic intermediate (see Chap. 7).

Generally, all processes based on acetylene, ethylene, and ethanol are more selective than the oxidation of saturated hydrocarbons. This is because, in the latter case, other oxidation products are formed in addition to acetaldehyde. Because of the great expense of separating the product mixture, such processes are economical only in large units and when all main and secondary products obtained in the process are utilized.

4.1. Production from Ethanol

For the production of acetaldehyde, ethanol can either be dehydrogenated or oxidized in the presence of oxygen. Between 1918 and 1939, dehydrogenation took precedence over oxidation because of the simultaneous production of hydrogen. Later, however, the catalytic vapor-phase oxidation of ethanol became the preferred process, probably because of the long catalyst life and the possibility of recovering energy.

**Dehydrogenation of Ethanol.** In the first work on ethanol dehydrogenation, published in 1886, ethanol was passed through glass tubes at 260 °C.

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2
\]

\[\Delta H = +82.5 \text{ kJ/mol}\]

Improved yields are obtained in the presence of catalysts such as platinum, copper, or oxides of zinc, nickel, or cobalt. In later patents, zinc and chromium catalysts [34], oxides of rare earth metals [35], and mixtures of copper and chromium oxides [36] have been reported. The lowest amounts of decomposition products are obtained using copper catalysts. Frequent regeneration of the catalysts is required, however.

**Process Description.** Ethanol vapor is passed at 260 – 290 °C over a catalyst consisting of copper sponge or copper activated with chromium oxide in a tubular reactor [37]. A conversion of 25 – 50 % per run is obtained. By washing with alcohol and water, acetaldehyde and ethanol are separated from the exhaust gas, which is mainly hydrogen. Pure acetaldehyde is obtained by distillation; the ethanol is separated from water and higher-boiling products by distillation and flows back to the reactor. The final acetaldehyde yield is ca. 90 %. Byproducts include butyric acid, crotonaldehyde, and ethyl acetate.

**Oxidation of Ethanol.** Oxidation of ethanol is the oldest and the best laboratory method for preparing acetaldehyde. In the commercial process, ethanol is oxidized catalytically with oxygen (or air) in the vapor phase.

\[
\text{CH}_3\text{CH}_2\text{OH}(g) + 1/2\text{O}_2(g) \rightarrow \text{CH}_3\text{CHO}(l) + \text{H}_2\text{O}(l)
\]

\[\Delta H = -242.0 \text{kJ/mol}\]

Copper, silver, and their oxides or alloys are the most frequently used catalysts [38].

For an example of a simultaneous oxidation – dehydrogenation process, see [39].

**Veba-Chemie Process** (Fig. 1). Ethanol is mixed with air and passed over a silver catalyst at 500 – 650 °C (c). The temperature depends on
the ratio of alcohol to air and the flow rate of the
gas through the catalyst. Alcohol conversion var-
ies between 50 and 70 % and the yield is between
97 and 99 % depending on the reaction condi-
tions. Acetaldehyde and unconverted alcohol are
removed from the waste gas by washing with cold
alcohol (e) and separated by fractional distillation
(h); after concentration the alcohol returns to the
reactor. Heat formed in the reaction is utilized for
steam production using a waste-heat recovery
system immediately after the reaction zone.

The waste gas consists mainly of nitrogen,
hydrogen, methane, carbon monoxide and carbon
dioxide; it is burned as lean gas with low calorific
value in steam generators. Small amounts of
acetic acid are obtained as a byproduct.

4.2. Production from Acetylene

The most important catalysts for the industrial
water addition (hydration) are mercury com-
ounds:

\[
C_2H_2(g) + H_2O(l) \xrightarrow{\text{Hg}^{2+}} H_2SO_4 \xrightarrow{\text{CH}_3\text{CHO}(l)} \Delta H = -138.2 \text{ kJ/mol}
\]

This method only succeeds industrially when
the polymerization and condensation products of
acetaldehyde formed in the acid medium are
eliminated. To achieve this, the Consortium für
elektrochemische Industrie in 1912 proposed a
process using excess acetylene at an elevated
temperature and removing the acetaldehyde
product immediately from the reaction liquid. At
the same time, the heat of reaction is removed by
distilling an appropriate amount of water. Sec-
ondary reactions, such as the oxidation of acetal-
dehyde to form acetic acid and carbon dioxide,
result in reduction of Hg\(^{2+}\) to metallic mercury. In
Western countries, acetaldehyde production from
acetylene has now been discontinued.

Wet Oxidation Process (Hoechst). The
wet oxidation process avoided direct handling
of the toxic mercury compounds. It was operated,
among others, by Wacker-Chemie until the
changeover to ethylene as the starting material
in 1962.

In this method, iron(III) sulfate is added to
reoxidize the mercury metal to the mercury(II)
salt, thus ensuring sufficient concentrations of
active catalyst. The acetylene reacts at 90 –
95 °C with the aqueous catalyst solution; be-
tween 30 and 50 % of the injected acetylene
reacts in one run. The gas emerging from the
reactor is cooled; mainly water and traces of
mercury are separated and returned to the reactor.
Acetaldehyde and water are condensed in addi-
tional coolers and the acetaldehyde finally is
washed out with water from the cycle gas which
has been cooled to 25 – 30 °C. An 8 – 10 %
aqueous acetaldehyde solution is obtained.
Nitrogen is introduced with the feed gas while
carbon dioxide is formed as a byproduct; to avoid
excessive accumulation, these gases are removed
by withdrawing a small stream of the cycle gas.
Iron(II) sulfate is formed in the reaction and is
oxidized in a separate reactor with 30 % nitric
acid at 95 °C. Pure acetaldehyde is obtained by
fractional distillation of the aqueous solution at
about 200 kPa. For further details of this process,
see [40].

Chisso Process [41]. The Chisso process
also uses sulfuric acid/mercury sulfate solution
as a catalyst. The acetylene reacts completely
with the catalyst solution at 68 – 78 °C and a
gauge pressure of 140 kPa. A combination of
pressure and vacuum process stages at low
temperature and without excess acetylene is
used; pure acetaldehyde can be isolated and
distilled by utilizing the heat of the reaction. As
in the Hoechst process, the catalyst can be
regenerated with nitric acid. Production of
acetaldehyde by this method was discontinued
at Chisso Corp. more than a decade ago.
**Production via Vinyl Ether.** REPE at BASF developed the process using vinyl ether [40]; it was operated in a pilot plant between 1939 and 1945. The use of toxic mercury compounds is avoided altogether. Methanol is added to acetylene at 150 – 160 °C and 1600 kPa in the presence of potassium hydroxide to form methyl vinyl ether [107-25-5]. The methyl vinyl ether is then hydrolyzed with dilute acid:

\[
C_2H_5 + CH_3OH \xrightarrow{KOH} CH_2OCH + CH_3 \xrightarrow{H_2O, H^+} CH_3OH + CH_3CHO
\]

**Production via Ethylidene Diacetate.** Addition of acetic acid to acetylene in the presence of mercury(II) salts yields ethylidene diacetate [542-10-9], CH_3CH(OCOCH_3)_2, which decomposes into acetaldehyde and acetic anhydride at 130 – 145 °C in the presence of acid catalysts (e.g., ZnCl_2). This process was developed by the Societe Chimique des Usines du Rhône on an industrial scale in 1914 but is now without importance.

### 4.3. Production from Ethylene

Ethylene is now the most important starting material for the production of acetaldehyde. Most of the present capacity works by the direct oxidation of ethylene (Wacker process).

#### 4.3.1. Direct Oxidation of Ethylene

This process was developed between 1957 and 1959 by Wacker-Chemie and Hoechst [42]. Formally, the reaction proceeds as follows:

\[
C_2H_4 + 1/2O_2 \rightarrow CH_2CHO + H_2O + H^+ + Cl^-
\]

An aqueous solution of PdCl_2 and CuCl_2 is used as catalyst. Acetaldehyde formation had already been observed in the reaction between ethylene and aqueous palladium chloride. This reaction is almost quantitative:

\[
C_2H_4 + PdCl_2 + H_2O \rightarrow CH_2CHO + Pd + 2HCl
\]

In the Wacker-Hoechst process, metallic palladium is reoxidized by CuCl_2, which is then regenerated with oxygen:

\[
Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl
\]

\[
2CuCl_2 + 1/2O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O
\]

Therefore only a very small amount of PdCl_2 is required for the conversion of ethylene. The reaction of ethylene with palladium chloride is the rate-determining step.

One- and two-stage versions of the process are on stream. In the one-stage method, an ethylene – oxygen mixture reacts with the catalyst solution. During the reaction a stationary state is established in which “reaction” (formation of acetaldehyde and reduction of CuCl_2) and “oxidation” (reoxidation of CuCl) proceed at the same rate. This stationary state is determined by the degree of oxidation of the catalyst, as expressed by the ratio \(c_{Cu^{2+}} / (c_{Cu^{2+}} + c_{Cu^+})\). In the two-stage process the reaction is carried out with ethylene and then with oxygen in two separate reactors. The catalyst solution is alternately reduced and oxidized. At the same time the degree of oxidation of the catalyst changes alternately. Air is used instead of pure oxygen for the catalyst oxidation.

**Reaction Mechanism.** The first step of the reaction is the complexation of ethylene to give a palladium ethylene complex

\[
[PdCl_4]^{2-} + H_2C = CH_2 = [(C_2H_4)PdCl_3]^- + Cl^-
\]

Kinetic studies of this reaction show that chloride ions have a inhibiting effect which is explained by the following substitution of a further chloride ligand by a water molecule:

\[
[(C_2H_4)PdCl_3]^- + H_2O = [(C_2H_4)PdCl_2(OH)]^- + H^+ + Cl^{-}
\]

Dissociation of hydrogen ions explains the inhibiting effect of acids:

\[
[(C_2H_4)PdCl_2(OH)]^- + H_2O = [(C_2H_4)PdCl_2(OH_2)]^- + H^+ + Cl^{-}
\]

It is assumed that the hydroxyl complex has the trans geometry. Evidence for the trans – cis isomerisation of this complex was revealed by a detailed kinetic study of the reaction. π-Bonded ethylene ligands in the trans position weaken the metal – chlorine bonds, so that the chloro ligand can be easily substituted by a water molecule from which a hydrogen ion dissociates.

\[
trans-[(C_2H_4)PdCl_2(OH)]^- + H_2O = [(C_2H_4)PdCl_2(OH_2)]^- + H^+ + Cl^{-}
\]

The OH^- ligand in the trans position is replaced by a Cl^- ion, leading to a cis complex:
\[ [(\text{C}_2\text{H}_4)\text{PdCl(OH)}_2]^--\text{H}^+\text{Cl}^- = \text{cis-}[((\text{C}_2\text{H}_4)\text{PdCl}_2\text{(OH)})]^--\text{H}_2\text{O} \]

The next reaction step is the formation of a σ-bonded hydroxyethylpalladium species. This reaction has been regarded as a cis ligand insertion reaction in which the OH⁻ ligand attacks the π-bonded olefin:

\[ \text{cis-}[(\text{C}_2\text{H}_4)\text{PdCl}_2\text{(OH)}]^-- = [\text{HOCH}_2\text{CH}_3\text{PdCl}_2]^-- \]

Hydride transfer to give an α-hydroxyethylpalladium complex is followed by reductive elimination, which is the rate-determining step:

\[ [\text{HOCH}_2\text{CH}_3\text{PdCl}_2]^-- = [\text{CH}_3\text{CH}^-\text{OH}]\text{PdCl}_2^- \]

\[ \text{CH}_3\text{CH}^-\text{OH}\text{PdCl}_2^- \rightarrow \text{CH}_3\text{CHO} + \text{Pd} + \text{H}^+ + 2\text{Cl}^- \]

For a detailed description, see [43]. The rate of reaction can be given by the following equation [44]:

\[ -\frac{d[\text{O}_2]}{dt} = \frac{k_{\text{cat}}}{{[\text{Pd}]}_0} \cdot \frac{[\text{O}_2]}{[\text{C}_2\text{H}_4]} \cdot \frac{[\text{H}_2\text{O}]}{[\text{Cl}^-]} \]

The rate of reaction is diminished by the acid formed in the reduction of palladium chloride. This can be prevented by buffering the acid with basic copper salts (copper oxychloride, copper acetate). Reformation of the basic copper salts takes place during catalyst oxidation.

**One-Stage Process** (Fig. 2). Ethylene and oxygen are charged into the lower part of the reaction tower (a); the catalyst is circulated via the separating vessel (b) by the airlift principle and thoroughly mixed with the gas. Reaction conditions are about 130 °C and 400 kPa. An acetaldehyde – water vapor mixture, together with unconverted gas, is withdrawn from the separating vessel; from this mixture the reaction products are separated by cooling (c) and washing with water (d); unconverted gas is returned to the reactor. A small portion is discharged from the cycle gas as exhaust gas to prevent accumulation of inert gases in the cycle gas; these inert gases are either introduced as contamination of the feed gas (nitrogen, inert hydrocarbons) or formed as by-products (carbon dioxide). A partial stream of catalyst is heated to 160 °C (m) to decompose byproducts that have accumulated in the catalyst.

Crude acetaldehyde obtained during washing of the reaction products is distilled in two stages. The first stage (g) is an extractive distillation with water in which lights ends having lower boiling points than acetaldehyde (chloromethane, chloroethane, and carbon dioxide) are separated at the top, while water and higher-boiling byproducts, such as acetic acid, crotonaldehyde, or chlorinated acetaldehydes, are withdrawn together with acetaldehyde at the bottom. In the second column (i) acetaldehyde is purified by fractional distillation.

**Two-Stage Process** (Fig. 3). Tubular reactors (a), (d) are used for both “reaction” and “oxidation”. The gases react almost completely in the presence of the catalyst. Reaction of ethylene takes place at 105 – 110 °C and 900 – 1000 kPa. Catalyst solution containing acetaldehyde is then

---

**Figure 2.** One-stage process
a) Reactor; b) Separating vessel; c) Cooler; d) Scrubber; e) Crude aldehyde tank; f) Cycle-gas compressor; g) Light-ends distillation; h) Condensers; i) Purification column; l) Product cooler; m) Regeneration
expanded in a flash tower (b) by reducing the pressure to atmospheric level. An acetaldehyde – water vapor mixture distills overhead while catalyst is sent via the pump (c) to the oxidation reactor (d), in which it reacts with oxygen at about 1000 kPa. As oxidation and reaction are carried out separately, no high-purity starting gas is required. Generally, air is used instead of oxygen. Oxygen conversion is almost complete; the exhaust air from (e) can be used as inert gas for plant use. The oxidized catalyst solution separated from exhaust air in the separator (e) is reused for the reaction with ethylene in (a).

Acetaldehyde – water vapor mixture from the flash tower (b) is preconcentrated in column (f) to 60 – 90% acetaldehyde by utilizing the heat of reaction. Process water discharged at the bottom of (f) is returned to the flash tower to maintain a constant catalyst concentration. A portion of the process water is used for scrubbing exhaust air (nitrogen from the “oxidation”) in (i) and exhaust gas (inert gas from the “reaction”) in (k) free of acetaldehyde. Scrubber water then flows to the crude aldehyde column (f).

A two-stage distillation of the crude acetaldehyde follows. In the first stage (l), low-boiling substances, such as chloromethane, chloroethane and carbon dioxide, are separated. In the second stage (o), water and higher-boiling byproducts, such as chlorinated acetaldehydes and acetic acid, are removed from acetaldehyde, and the latter is obtained in pure form overhead. Chlorinated acetaldehydes become concentrated within the column as medium-boiling substances and are discharged laterally. From this mixture, monochloroacetaldehyde can be obtained as the hemihydrate. Residual byproducts can be returned to the catalyst for oxidative decomposition. This oxidative self-purification is supported by thermal treatment of a partial stream of catalyst at about 160 – 165 °C (regeneration, r).

When gas mixtures obtained in naphtha cracking processes are used as raw material, conventional towers are used as reactors instead of coiled pipes; So far, these processes have not been developed industrially. Such mixtures contain 30 – 40% ethylene in addition to inert hydrocarbons and hydrogen [45].

**Comparison of the Two Methods.** In both one- and two-stage processes the acetaldehyde yield is about 95% and the production costs are virtually the same. The advantage of using dilute gases in the two-stage method is balanced by higher investment costs. Both methods yield chlorinated hydrocarbons, chlorinated acetaldehydes, and acetic acid as byproducts. Generally, the choice of method is governed by the raw material and energy situations as well as by the availability of oxygen at a reasonable price.

---

**Figure 3. Two-stage process**

a) Reactor; b) Flash tower; c) Catalyst pump; d) Oxidation reactor; e) Exhaust-air separator; f) Crude-aldehyde column; g) Process-water tank; h) Crude-aldehyde container; i) Exhaust-air scrubber; k) Exhaust-gas scrubber; l) Light-ends distillation; m) Condensers; n) Heater; o) Purification column; p) Cooler; q) Pumps; r) Regeneration
Balance of Reaction and Side Products.  
The yield in both type of process is nearly the same. The balance of the two stage process is as follows:  

100 parts of ethylene gives:  

- 95 parts acetaldehyde  
- 1.9 parts chlorinated aldehydes  
- 1.1 parts unconverted ethylene  
- 0.8 parts carbon dioxide  
- 0.7 parts acetic acid  
- 0.1 parts chloromethane  
- 0.1 parts ethyl chloride  
- 0.3 parts ethane, methane, crotonaldehyde and other minor side products  

The chlorinated aldehydes consist of chloroacetaldehyde, dichloroacetaldehyde, trichloroacetaldehyde, and 2-chloro-2-butenal.

Process Variant.  
An interesting variant of the process, although so far of no technical importance, uses glycol as the reaction medium. The cyclic acetal of acetaldehyde, namely the easily hydrolyzable 2-methyl-1,3-dioloxane, is obtained. An advantage of this method is the high rate of reaction [46].

Construction Materials.  
During process development, serious problems have been caused by the extremely corrosive aqueous CuCl2 – PdCl2 solution. These problems have been solved in the two-stage process either by constructing parts in contact with the catalyst solution entirely from titanium or by lining those parts with the metal. In the one-stage process, the reactor is lined with acid-proof ceramic material, the tubing is made of titanium, and certain other parts are of tantalum.

Waste Air.  
The waste air from the oxidation process contains small amounts of unconverted ethylene, some acetaldehyde, and side products from the reaction such as ethane, chloromethane, chloroethane, and methane. In Germany the waste air must be purified of these side products to meet the criteria of TA-Luft [47]. The byproducts are oxidized over a chromium oxide catalyst. The hydrogen chloride generated is removed by washing, so that the waste air contains mainly carbon dioxide.

Wastewater.  
Side products of the oxidation process that enter the wastewater are acetic acid, crotonaldehyde and chlorinated aldehydes. Some of the chlorinated aldehydes are highly toxic and show high antimicrobial activity. Therefore they must be treated before entering the wastewater plant to render them biologically degradable. Cleavage of organic chlorine by alkaline hydrolysis is a possible method. If the chlorinated compounds can not be destroyed the wastewater has to be incinerated.

4.3.2. Acetaldehyde as Byproduct  
Acetaldehyde is also formed in the production of vinyl acetate from ethylene or acetylene (→ Vinyl Esters). It is separated by distillation and is normally converted to acetic acid for reuse. In one version of the method starting from ethylene, vinyl acetate and acetaldehyde are obtained in a molar ratio of 1:1. This makes the process nearly self-sufficient in acetic acid.

4.3.3. Isomerization of Ethylene Oxide  
Research was carried out on this process [48] before adopting the direct oxidation of ethylene. Catalysts were Al2O3, SiO2, and acid salts of mineral acids, such as sulfuric acid, phosphoric acid, or molybdic acid. Yields of 90 – 95 % have been reported, but the process has not gained industrial importance.

4.4. Production from C1 Sources  
Since the increases in oil price in 1973/74 and 1977, C1 material has gained interest as a feedstock for organic chemicals and as a substitute for petrochemicals. However, for acetaldehyde production, C1 material seems to be of minor importance because most of the classical acetaldehyde derivatives can be made from C1 sources.

Production Directly from Synthesis Gas.  
Acetaldehyde is formed with low selectivity and a yield of ca. 30 % from synthesis gas, together with acetic acid, ethanol, and saturated hydrocarbons, mainly methane. Catalysts are cobalt
and rhodium compounds activated by iodine compounds or magnesium chloride and supported on a silicate carrier [49]. There is so far no industrial use of this process.

**Production via Methanol, Methyl Acetate, or Acetic Anhydride.** *Hydroformylation of methanol* with CO/H₂ has been well known since the discovery of the oxo process [50]. It takes place in the presence of hydroformylation catalysts, such as cobalt, nickel, and iron salts (e.g., CoBr₂, CoI₂) or the corresponding metal carbonyls, at increased temperature (180 – 200 °C) and high pressure (30 – 40 MPa). An acetaldehyde selectivity of 80% or more has been claimed using an iron – cobalt carbonyl or alternatively a cobalt – nickel catalyst in the presence of tertiary amines, phosphines, or nitriles as the catalyst [51, 52].

Similarly, high selectivity has been claimed for the *hydrocarbonylation of methyl acetate* with palladium or rhodium catalysts in the presence of tertiary phosphines and iodine compounds as well as cobalt – ruthenium catalysts in the presence of methyl and sodium iodides [53].

Some patents describe the formation of acetaldehyde by *reduction of acetic anhydride* with hydrogen over palladium or platinum on a carrier at low pressures and moderate temperatures [54]. If the importance of acetaldehyde as an organic intermediate were to decrease in the future as outlined in Chapter 8, this method might be of some interest for the economical production of small quantities of acetaldehyde.

### 4.5. Production from Hydrocarbons

Acetaldehyde is a byproduct of the production of acrolein, acrylic acid, and propene oxide from propene. It is also formed in the oxidation of saturated hydrocarbons (e.g., propane or butane) in the gas phase as operated by Celanese in the United States [55] (→ Acetic Acid).

### 5. Quality and Analysis

High demands on acetaldehyde purity generally are made; a typical specification is:

<table>
<thead>
<tr>
<th>Component</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>more than 99.5 wt %</td>
</tr>
<tr>
<td>Acid (as acetic acid)</td>
<td>less than 0.1 wt %</td>
</tr>
<tr>
<td>Water</td>
<td>less than 0.02 wt %</td>
</tr>
<tr>
<td>Chlorine</td>
<td>less than 30 mg/kg</td>
</tr>
<tr>
<td>Dry residue</td>
<td>less than 10 mg/kg</td>
</tr>
</tbody>
</table>

The *acid content* is determined directly by titration, *water content* using the Karl Fischer reagent or empirically from the cloud point of a carbon disulfide – acetaldehyde mixture, and *chlorine content* (mostly in the form of organic chlorine compounds) by combustion in a hydrogen stream and determination of the hydrochloric acid in the condensate.

### 6. Storage and Transportation

#### 6.1. Storage

For storage of acetaldehyde, the national regulations must be observed. In *Germany* the ordinance on operational safety (Betriebssicherheitsverordnung) applies, under which acetaldehyde is classified as highly inflammable liquid (F⁺). In the *USA*, loading and storage of acetaldehyde are governed by the EPA.

In *Japan* the Fire Defense Law and the supplement “Cabinet Order for Control of Dangerous Articles” applies. According to these regulations, outer storage tanks must not be made of copper, magnesium, silver, mercury, or alloys of these metals. They must be equipped with cooling facilities in order to keep the temperature below 15 °C, and also with an inert-gas sealing system.

For safety data, see Chapter 2.

#### 6.2. Transportation

**International Regulations.** Acetaldehyde is classified as a flammable liquid. Transportation is governed by:

- IMDG Code (sea transport): class 3, UN 1089, packing group I
- RID (rail): class 3, UN 1089, packing group I
- ADR (road): class 3, UN 1089, packing group I
- ADNR (inland waterways), class 3, UN 1089, packing group I
IATA-DGR (air transportation): class 3, UN 1089, packing group I, PAC forbidden, CAC packing instruction 304, 30 L max.

National Regulations. Germany: GGVSE (road and rail); GGVSee (sea). USA: Regulations of the U.S. Department of Transportation: CFR 49.

Types and sizes of packaging and containers are recommended by the regulations mentioned above.

6.3. Other Regulations

In Germany, any accidental release of acetaldehyde into the air, water, or soil must be reported to the appropriate authorities according to the ordinance on operational safety (Betriebssicherheitsverordnung) or the regulations on units for storing, filling, and moving materials dangerous to water supplies (Hazardous Incident Ordinance, Störfallverordnung, 2005).

In the United States, a similar regulation applies according to the Comprehensive Environmental Response, Compensation, and Liability Act of 1980. Incidents must be reported to the National Response Center for Water Pollution.

In Japan, acetaldehyde is specified as an Offensive Odor Material by the Offensive Odor Control Law. Under this law a district of dense population is specified, for which the concentration of the material in the air is limited. The maximum level of acetaldehyde allowed at the boundary of the factory or place where acetaldehyde is handled is 0.5 ppm.

Environmental problems are dealt with by the respective national laws (see above). If acetaldehyde is highly diluted with water it can easily be degraded biologically. In higher concentrations it kills bacterial flora.

7. Economic Aspects

Today the most important production process worldwide is the direct oxidation of ethylene. In Western Europe there is also some capacity for the production of acetaldehyde by oxidation of ethanol (7 %) and hydration of acetylene (17 %). In South America the entire capacity for production of acetaldehyde is based on the oxidation of ethanol.

However, the demand for acetaldehyde worldwide has continued to decrease primarily as a result of less consumption for acetic acid manufacture, as the industry continues to move toward the more efficient methanol carbonylation process. All manufacture of acetic acid from acetaldehyde in North America has been discontinued, and in Europe significant capacity for this transformation has been permanently shut down. Acetaldehyde use for acetic acid manufacture in Asia continues but is under pressure and will decline because of the establishment of methanol carbonylation technology. Since 1995, some 360 000 t of acetaldehyde capacity has been shut down in Western Europe, and Mexico has eliminated its acetaldehyde capacity. New acetaldehyde capacity has been installed in China, but this is the only area where new capacity has been added. Further carbonylation capacity will be added between 2006 and 2008, but afterward the demand for acetaldehyde for acetic acid will eventually be phased out. Capacity in China is expected to be around 860 000 t by 2008 and is expected to remain at those levels for at least five more years.

Table 2 gives production data for acetaldehyde.

Important producers and their production capacities (10³ t) are listed in the following [56]:

<table>
<thead>
<tr>
<th>Company</th>
<th>Capacity (10³ t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celanese Chemicals Europe GmbH, Germany</td>
<td>120</td>
</tr>
<tr>
<td>Eastman Chemical Company, USA</td>
<td>225</td>
</tr>
<tr>
<td>ECROS, SA, Spain</td>
<td>90</td>
</tr>
<tr>
<td>Japan Aldehyde Company Ltd., Japan</td>
<td>69</td>
</tr>
<tr>
<td>Ilin Chemical Industrial Company, China</td>
<td>180</td>
</tr>
<tr>
<td>Kyowa Yuka Company Ltd., Japan</td>
<td>61</td>
</tr>
<tr>
<td>Showa Denko K.K., Japan</td>
<td>300</td>
</tr>
<tr>
<td>Sinopec Yangzi Petrochemical Co., China</td>
<td>78 (400 planned)</td>
</tr>
<tr>
<td>Wacker Chemie AG, Germany</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 2. Production of acetaldehyde (10³ t) [56]

<table>
<thead>
<tr>
<th>Year</th>
<th>USA</th>
<th>W. Europe</th>
<th>Mexico</th>
<th>Japan</th>
<th>China</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>283</td>
<td>603</td>
<td>190</td>
<td>384</td>
<td></td>
<td>1460</td>
</tr>
<tr>
<td>1995</td>
<td>111</td>
<td>668</td>
<td>271</td>
<td>395</td>
<td>400</td>
<td>1845</td>
</tr>
<tr>
<td>2000</td>
<td>155</td>
<td>370</td>
<td>113</td>
<td>401</td>
<td>400</td>
<td>1439</td>
</tr>
<tr>
<td>2003</td>
<td>142</td>
<td>212</td>
<td>57</td>
<td>362</td>
<td>500</td>
<td>1273</td>
</tr>
</tbody>
</table>
8. Polymers of Acetaldehyde

8.1. Paraldehyde

Paraldehyde, 2,4,6-trimethyl-1,3,5-trioxane \([123-63-7]\), \(\text{C}_6\text{H}_{12}\text{O}_3\), \(M_r\) 132.161, is a cyclic trimer of acetaldehyde:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH} \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH} \\
\text{CH}_3
\end{array}
\]

**Properties.** Paraldehyde is colorless and has an ethereal, penetrating odor. bp 124.35 °C

mp 12.54 °C

Critical temperature \(t_{\text{crit}}\) 290 °C

Solubility in 100 g water at 13 °C 12 g

at 75 °C 5.8 g

In the solid state, four different crystal forms exist; transition points: 230.3 K, 147.5 K, 142.7 K.

Paraldehyde is miscible with most organic solvents.

**Density** \(d_{20}^0\) 0.9923

**Viscosity** at 20 °C 1.4049

**Heat of combustion at constant pressure** 3405 kJ/mol

**Heat capacity** \(c_p\) at 25 °C 1.947 J g⁻¹ K⁻¹

**Entropy** \(S\) at 25 °C 2.190 J g⁻¹ K⁻¹

**Free energy** \(G\) at 25 °C 276.4 J/g

**Heat of vaporization** 41.4 kJ/mol

**Latent heat of melting** 104.75 J/g

**Heat of formation from acetaldehyde** (calculated from combustion enthalpies) –113.0 kJ/mol

The equilibrium 3 acetaldehyde = paraldehyde is 94.3 % on the paraldehyde side at 150 °C.

**Production.** Paraldehyde is produced from acetaldehyde in the presence of acid catalysts, such as sulfuric acid, phosphoric acid, hydrochloric acid, or acid cation exchangers. In the homogeneous reaction, acetaldehyde is added, with stirring and cooling, to paraldehyde containing a small amount of sulfuric acid. After the addition is completed, stirring is continued for some time to establish the equilibrium; the sulfuric acid is exactly neutralized with a sodium salt, such as sodium acetate, sodium carbonate, or sodium bicarbonate; the reaction mixture is separated into acetaldehyde, water, and paraldehyde by fractional distillation [57].

For continuous production, liquid acetaldehyde at 15 – 20 °C or acetaldehyde vapor at 40 – 50 °C is passed over an acid cation exchanger [58]. Conversion is greater than 90 %. Acetaldehyde and paraldehyde are separated by distillation. For depolymerization, acetaldehyde is slowly distilled off in the presence of acid catalysts. Paraldehyde also can be decomposed in the gas phase. Catalysts are HCl, HBr, \(\text{H}_3\text{PO}_4\), or cation exchangers. The reaction is first order. Other catalysts described in the literature are \(\text{Al}_2\text{O}_3\), \(\text{SiO}_2\), \(\text{ZnSO}_4\), and \(\text{MgSO}_4\) [59].

**Uses.** Paraldehyde is used in chemical synthesis as a source of acetaldehyde whereby resin formation and other secondary reactions are largely eliminated. Such synthetic reactions are, for instance, used for the production of pyridines and chlorination of chloral. Between 1939 and 1945 paraldehyde was used as a motor fuel.

**Production.** Paraldehyde is produced from acetaldehyde in the presence of acid catalysts, such as sulfuric acid, phosphoric acid, hydrochloric acid, or acid cation exchangers. In the homogeneous reaction, acetaldehyde is added, with stirring and cooling, to paraldehyde containing a small amount of sulfuric acid. After the addition is completed, stirring is continued for some time to establish the equilibrium; the sulfuric acid is exactly neutralized with a sodium salt, such as sodium acetate, sodium carbonate, or sodium bicarbonate; the reaction mixture is separated into acetaldehyde, water, and paraldehyde by fractional distillation [57].

**Production.** Paraldehyde is produced from acetaldehyde in the presence of acid catalysts, such as sulfuric acid, phosphoric acid, hydrochloric acid, or acid cation exchangers. In the homogeneous reaction, acetaldehyde is added, with stirring and cooling, to paraldehyde containing a small amount of sulfuric acid. After the addition is completed, stirring is continued for some time to establish the equilibrium; the sulfuric acid is exactly neutralized with a sodium salt, such as sodium acetate, sodium carbonate, or sodium bicarbonate; the reaction mixture is separated into acetaldehyde, water, and paraldehyde by fractional distillation [57].

8.2. Metaldehyde

Metaldehyde [9002-91-9], \(\text{C}_8\text{H}_{16}\text{O}_4\), \(M_r\) 176.214, is the cyclic tetramer of acetaldehyde:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\text{O} \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{O}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH} \\
\text{CH}_3
\end{array}
\]

**Properties.** Metaldehyde forms tetragonal prisms, \(mp\) (closed capillary) 246.2 °C, sublimation temperature (decomp.) 115 °C, heat of combustion at constant volume 3370 kJ/mol.

Metaldehyde is insoluble in water, acetone, acetic acid, and carbon disulfide.

Depolymerization of metaldehyde to acetaldehyde begins at 80 °C, and is complete above 200 °C. Depolymerization takes place faster and at lower temperatures in the presence of acid catalysts, such as dilute \(\text{H}_2\text{SO}_4\) or \(\text{H}_3\text{PO}_4\). Metaldehyde does not show the typical acetaldehyde reactions. It is stabilized by ammonium carbonate or other weakly basic compounds which neutralize acidic potential catalysts.

**Production.** Metaldehyde is obtained in addition to large amounts of paraldehyde during...
polymerization of acetaldehyde in the presence of HBr and alkaline earth metal bromides, such as CaBr₂, at temperatures below 0 °C. However, yields are scarcely higher than 8%. Yields of 14 – 20% have been reported when working in the presence of 7 – 15% of an aliphatic or cyclic ether at 0 – 20 °C [60]. Insoluble metaldehyde is filtered out. Acetaldehyde is then distilled from the filtrate following depolymerization of the paraldehyde and is returned to the polymerization. Recycling of the large amounts of acetaldehyde results in losses that increase the process costs.

Uses. Metaldehyde in pellet form is marketed as a dry fuel (Meta). Mixed with a bait, metaldehyde is used as a molluscicide.

8.3. Polyacetaldehyde

Polyacetaldehyde [9002-91-9] is a high-molecular-mass polymer with an acetal structure (polyoxymethylene structure):

\[
\text{CH}_3 - \text{O} - \text{CH} - \text{O} - \text{CH}_2 - \text{O} -
\]

By using cationic initiators, mainly an amorphous polymer is obtained. Temperatures below −40 °C are preferred in this case. Above −30 °C, mainly paraldehyde and metaldehyde are produced. The initiator activity also depends on the solvent used. Suitable initiators include H₃PO₄ in ether and pentane, as well as HCl, HNO₃, CF₃COOH, AlCl₃ in ether, and particularly BF₃ in liquid ethylene [61]. Al₂O₃ and SiO₂ also seem to be good initiators [62].

The polymer has a rubber-like consistency and is soluble in common organic solvents. It depolymerizes at room temperature, liberating acetaldehyde. It evaporates completely within a few days or weeks. Acidic compounds accelerate depolymerization, and amines (e.g., pyridine) stabilize polyacetaldehyde to a certain extent. A complete stabilization (as, for instance, in the case of polyformaldehyde) has not yet been achieved, so the polymer is still of no practical importance.

Copolymers with propionaldehyde, butyraldehyde, and allylacetaldheyde also have been produced [63]. Crystalline, isotactic polymers have been obtained at low temperatures (for example, −75 °C) by using anionic initiators [64]. Suitable initiators are alkali metal alkoxides, alkali metals, or metal alkyls in hydrocarbon solvents. The products are insoluble in common organic solvents but have an acetal structure like the amorphous polymers' [65]. Polymerization of acetaldehyde to poly (vinyl alcohol), which in contrast to polyacetaldehyde has a pure carbon backbone, has not yet been achieved [66].

9. Toxicology and Occupational Health

Acetaldehyde. At higher concentrations (up to 1000 ppm), acetaldehyde irritates the mucous membranes. The perception limit of acetaldehyde in air is in the range between 0.07 and 0.25 ppm [67, 68]. At such concentrations the fruity odor of acetaldehyde is apparent. Conjunctival irritations have been observed after a 15-min exposure to concentrations of 25 and 50 ppm [69], but transient conjunctivitis and irritation of the respiratory tract have been reported after exposure to 200 ppm acetaldehyde for 15 min [69, 70]. The penetrating odor, the low perception limit, and the irritation that acetaldehyde causes, give an effective warning so that no serious cases of acute intoxication with pure acetaldehyde have been reported. Acute acetaldehyde intoxication can also be observed following combined ingestion of disulfiram (Antabuse) and ethanol [73]. In animal experiments at high concentrations (3000 – 20 000 ppm), pulmonary edema and a narcotic effect become evident. The clinical course is similar to alcohol intoxication. Death occurs by breath paralysis or – with retardation – by pulmonary edema.

For rats, the LC₅₀ (30 min inhalation) is 20 500 ppm [71]. No studies on subchronic or chronic toxicity of acetaldehyde in humans are available. Investigations of sister chromatid exchange in cell cultures [72] and in human lymphocytes [74] and studies of single- and double-strand breaks in human lymphocytes incubated with acetaldehyde [75] have revealed mutagenic effects of acetaldehyde. Long-term exposures of Syrian golden hamsters to concentrations in the range 1650 – 2500 ppm have resulted in inflammatory hyperplastic and
metaplastic alterations of the upper respiratory tract with an increase in carcinomas of the nasal mucosa and the larynx [76]. Male and female Wistar rats were exposed to aldehyde concentrations of 0 ppm, 750 ppm, 1500 ppm for 6 h daily, 5 d per week for 52 weeks. In the highest dose group, the initial aldehyde concentration of 3000 ppm was reduced to 1000 ppm in the course of the study due to toxic effects. The dose-dependent effects found were increased mortality in all dose groups and delayed growth in the middle- and highest-dose group. Adenocarcinomas were observed at all three investigated concentrations. An increased rate of squamous epithelial carcinomas was only seen at 1500 ppm or more. Histological signs of irritation were observed in the larynx region in most animals from the medium- and high-dose groups [77]. Concomitant exposure to acetaldehyde also considerably increases the number of tracheal carcinomas induced by instillation of benzo[a]pyrene [72]. This suggests that chronic tissue injury is a prerequisite for tumor formation by acetaldehyde. Tumors probably do not develop if doses are not sufficient to cause tissue necrosis. In male Wistar rats exposed to 150 ppm or 500 ppm for 6 h per day, 5 d per week for 4 weeks, morphological changes in the olfactory epithelium were observed in the high-dose group [78]. However, long-term toxicity data at lower exposure concentrations are not yet available.

Currently, the TLV is 25 ppm (STEL/ceiling value) [79], and the MAK is 50 ppm [80]; the latter value is preliminary. At 50 ppm acetaldehyde, no irritation or local tissue damage in the nasal mucosa is observed. Because the mechanism of action is assumed to be analogous to that of formaldehyde, acetaldehyde is regarded as a suspected carcinogen [80].

When taken up by the organism, acetaldehyde is metabolized rapidly in the liver to acetic acid. Only a small proportion is exhaled unchanged. After intravenous injection, the half-life in the blood is approximately 90 s [81].

**Paraldehyde** acts as a sedative with few side effects. Ingested paraldehyde partly is metabolized to carbon dioxide and water and partly is exhaled unchanged. It generates an unpleasant odor in the expired air and therefore is not much used.

**Metaldehyde** decomposes slowly to acetaldehyde in the presence of acids, so ingestion may cause irritation of the gastric mucosa with vomiting. As characteristic signs of a metaldehyde intoxication, especially in children, heavy convulsions (sometimes lasting several days) have been reported, with lethal outcomes, after ingestion of several grams of metaldehyde [82]. For these reasons, those molluscicides and solid fuels which contain metaldehyde must be kept away from children.

**References**

**General References**

1. Beilstein 1 594; 1, 1st suppl., 1, 321; 1, 2nd suppl., 1, 654; 1, 2nd suppl., 1, 654; 1, 3rd suppl., 1, 2617; 1, 4th suppl., 3094.
5. R. Sieber in [3]: pp. 659 and 668.

**Specific References**

Further Reading


