Acetaldehyde

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1. Introduction

Acetaldehyde (ethanal), CH₃CHO [*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, C_2H_4O, M_r 44.054, is a colorless liquid with a pungent, suffocating odor that is slightly fruity when diluted.

bp at 101.3 kPa	20.16 °C
mp	−123.5 °C
Critical temperature t_{crit}	181.5 °C
other values	187.8 °C [12], 195.7 °C [13]
Critical pressure p_{crit}	6.44 MPa
other values	5.54 MPa [12], 7.19 MPa [13]
Relative density	$d_4^t = 0.8045 - 0.001325 \cdot t$
	(t in °C) [3]
Refractive index	$n_D^t = 1.34240 - 0.0005635 \cdot t$
	(t in °C) [14]
Molar volume of the gas	
at 101.3 kPa and 20.16 °C	23.40 L/mol
at 25.0 °C	23.84 L/mol
For dependence on T (293.32 – 800 K) and p (0.1 – 30 MPa), see [15].	
Specific volume of the vapor	
at 20.16 °C	0.531 m³/kg
at 25.0 °C	0.541 m³/kg
Vapor density (air = 1)	1.52

Vapor pressure

t, °C	−20	−0.27	5.17	14.76	50	100
p, kPa	16.4	43.3	67.6	82.0	279.4	1014.0

For further values between −60 and +180 °C, see [14]

Viscosity of liquid η	
at 9.5 °C	0.253 mPa · s
at 20 °C	0.21 mPa · s
Viscosity of vapor η	
at 25 °C	86×10^{-4} mPa · s
For further values between 35.0 and 77.8 °C and between 0.13 and 0.40 kPa, see [16].	
Surface tension γ at 20 °C	21.2×10^{-2} mN cm^{-1}
Dipole moment (gas phase)	2.69 ± 2 % D [12]
Dielectric constant	
of liquid at 10 °C	21.8
of vapor at 20.16 °C, 101.3 kPa	1.0216

Heat capacity of liquid	
c_p (l) at 0 °C	2.18 J g^{-1} K^{-1}
at 20 °C	1.38 J g^{-1} K^{-1}
For further values between −80 °C (c_p = 1.24 J g^{-1} K^{-1}) and +120 °C (c_p = 1.50 J g^{-1} K^{-1}), see [17].	
Heat capacity of vapor	
c_p (g) at 25 °C, 101.3 kPa	1.24 J g^{-1} K^{-1}
For dependence on temperature (nonlinear) between 0 °C (c_p = 1.17 J g^{-1} K^{-1}) and 1000 °C (c_p = 2.64 J g^{-1} K^{-1}), see [17].	
c_p/c_v (= ϰ) at 30 °C, 101.3 kPa 1.145 [18]	
Thermal conductivity	
of liquid at 20 °C	0.174 J m^{-1} s^{-1} K^{-1};
for more values, see [19]	
of vapor at 25 °C	1.09×10^{-2} J m^{-1} s^{-1} K^{-1}
for further values, see [20].	
Cubic expansion coefficient per K (0 – 20 °C)	0.00169
Heat of combustion of liquid at constant p	1168.79 (1166.4 [12]) kJ/mol
Heat of solution in water (infinite dilution)	17 906 J/mol
Latent heat of fusion	3246.3 J/mol
Latent heat of vaporization at 20.2 °C 25.73 kJ/mol	
other values	27.2 [21], 30.41, 27.71 [12], 26.11 [22] kJ/mol
For dependence on temperature (nonlinear) between -80 °C (32.46 kJ/mol) and 182 °C (0 kJ/mol), see [17].	

Heat of formation ΔH from the elements at 25 °C for gaseous acetaldehyde

    −166.47 (−166.4 [21]) kJ/mol

For dependence of heat of formation for gaseous and liquid acetaldehyde, and enthalpy of vaporization on temperature up to 800 K and 30 MPa, see [15].

Gibbs free energy of formation ΔG from elements	
at 25 °C for gaseous acetaldehyde	−133.81 kJ/mol
other values	133.72 [12], 132.9 [21] kJ/mol
Entropy for gaseous acetaldehyde	
at 25 °C	265.9 J mol^{-1} K^{-1}
Entropy for liquid acetaldehyde	
at 20.16 °C	172.9 J mol^{-1} K^{-1}
Entropy of vaporization	
at 20.16 °C	91.57 J mol^{-1} K^{-1}
First ionization potential	10.5 eV
Dissociation constant at 0 °C	0.7×10^{-14} mol/L
	($H_3CCHO^- H_2CCHO + H^+$)

For the second virial coefficient of the equation of state for gaseous acetaldehyde at 31 °C, 66 °C, and 85 °C, see [23].

Acetaldehyde is completely miscible with water and most organic solvents. It forms no azeotrope with water, methanol, ethanol, acetone, acetic acid, or benzene. Binary azeotropes are formed with butane (bp −7 °C, 84 wt % of butane) and diethyl ether (bp 18.9 °C, 23.5 wt % of ether).

Other Physical Data. Compressibility and viscosity at higher pressure are given in [24], vapor pressure of aqueous acetaldehyde solutions

in [25]. For solubility of carbon dioxide, acety-lene, 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) $-20\,^{\circ}$C ($-40\,^{\circ}$C according to the safety regulations of the Berufsgenossenschaft der Chemischen Industrie, Federal Republic of Germany). Ignition temper-ature (DIN 51 794; ASTM D 2155 – 66) 140 $^{\circ}$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 $^{\circ}$C acetalde-hyde 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 ($\rightarrow$ 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 ethyl-ene glycol and acetaldehyde, and 2-methyl-1,3-dioxane from 1,3-propanediol.

Aqueous *sodium bisulfite* solution and acetal-dehyde give a crystalline adduct from which acetaldehyde can be liberated. Dry *ammonia* forms crystalline acetaldehyde ammonia. Acet-aldehyde and *hydrocyanic acid* react to give lactonitrile (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] ($\rightarrow$ 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*], $CH_3CH(OH)CH_2CHO$. At increased temperatures, water is cleaved easily from this acetaldol, forming crotonaldehyde ($\rightarrow$ Aldehydes, Aliphatic). Fur-ther condensation under more stringent condi-tions to form aldehyde resins (e.g., synthetic shellac) now has no industrial importance.

Urea and acetaldehyde condense in the pres-ence of H_2SO_4 to form crotonylidenediurea (6-methyl-4-ureidohexahydropyrimidin-2-one [*1129-42-6*]), which is used as a long-term nitrogen fertilizer ($\rightarrow$ 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 pro-duction of pentaerythritol from acetaldehyde and a fourfold amount of formaldehyde in the pres-ence of $Ca(OH)_2$ or NaOH is very important industrially ($\rightarrow$ Alcohols, Polyhydric).

3.3. Reaction with Nitrogen Compounds

With primary amines, Schiff bases, $CH_3CH{=}NR$, are formed. Nitrogen compounds such as hydroxylamine, hydrazine, phenylhydra-zine, and semicarbazide react with acetaldehyde to give easily crystallizable compounds that are used for the analytical determination and char-acterization of aldehydes (semicarbazone, *mp* 162 – 163 $^{\circ}$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 Mn^{2+} salts, acetic acid is obtained from acetaldehyde monoperacetate, and in the presence of Co^{2+} and Cu^{2+} salts, acetic anhydride can be formed.

Oxidation with nitric acid gives glyoxal (→Glyoxal and → Glyoxylic Acid). Halogenated acetaldehydes are prepared by halogenation.
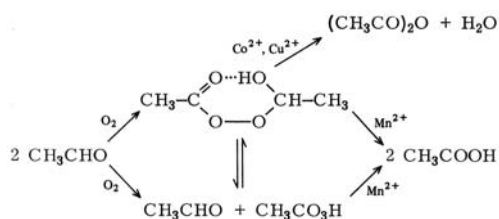
Mono-, di-, and trichloroacetaldehydes (→ Chloroacetaldehydes) and tribromoacetaldehyde (bromal) are useful for producing insecticides (e.g., DDT, DDD), pharmaceuticals, and dyes.

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 1. Consumption of acetaldehyde (10^3 t) in 2003 [56]

Product	USA	Mexico	W. Europe	Japan	Total
Acetic acid/acetic anhydride		11	89	47	147
Acetate esters	35	8	54	224	321
Pentaerythritol	26		43	11	80
Pyridine and pyridine bases	73		10	*	83
Peracetic acid	23			*	23
1,3-Butylene glycol	14			*	14
Others	5	3	10	80	98
Total	176	22	206	362	766

* 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.

$$CH_3CH_2OH(l) \rightarrow CH_3CHO(l) + H_2(g)$$
$$\Delta H = +82.5 \ kJ/mol$$
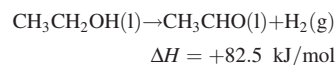
Improved yields are obtained in the presence of catalysts such as platinum, copper, or oxides of zinc, nickel, or cobalt. In later patents, zinc and chromium catalysts [34], oxides of rare earth metals [35], and mixtures of copper and chromium oxides [36] have been reported. The lowest amounts of decomposition 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.

$$CH_3CH_2OH(g) + 1/2O_2(g) \rightarrow CH_3CHO(l) + H_2O(l)$$
$$\Delta H = -242.0 kJ/mol$$
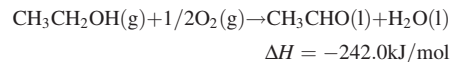
Copper, silver, and their oxides or alloys are the most frequently used catalysts [38].

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
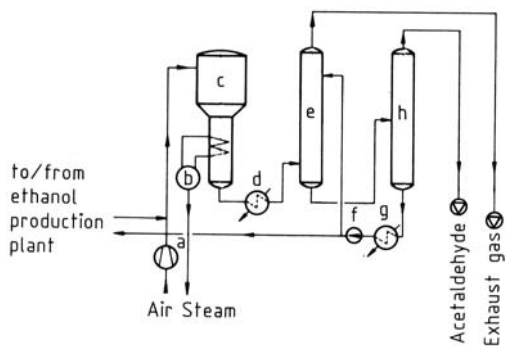
**Figure 1.** Acetaldehyde production by the Veba-Chemie process
a) Air compressor; b) Heat recovery system; c) Reactor; d) Cooler; e) Waste-gas scrubber; f) Washing-alcohol and return pump; g) Cooler; h) Acetaldehyde rectification

the ratio of alcohol to air and the flow rate of the gas through the catalyst. Alcohol conversion varies between 50 and 70 % and the yield is between 97 and 99 % depending on the reaction conditions. 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 compounds:

$$C_2H_2 \, (g) + H_2O \, (l) \xrightarrow[H_2SO_4]{Hg^{2+}} CH_3CHO \, (l) \, \Delta H = -138.2 \, kJ/mol$$
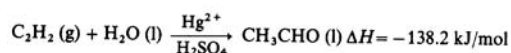
This method only succeeds industrially when the polymerization and condensation products of acetaldehyde formed in the acid medium are eliminated. To achieve this, the Consortium für elektrochemische Industrie in 1912 proposed a process using excess acetylene at an elevated temperature and removing the acetaldehyde product immediately from the reaction liquid. At the same time, the heat of reaction is removed by distilling an appropriate amount of water. Secondary reactions, such as the oxidation of acetaldehyde 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; between 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 additional 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. REPPE 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:

$$C_2H_2 + CH_3OH \xrightarrow{KOH} CH_3OCH=CH_2 \xrightarrow[+CH_3CHO]{H_2O,\ H^+} CH_3OH$$
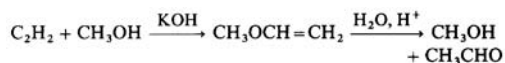
Production via Ethylidene Diacetate. Addition of acetic acid to acetylene in the presence of mercury(II) salts yields ethylidene diacetate [*542-10-9*], $CH_3CH(OCOCH_3)_2$, which decomposes into acetaldehyde and acetic anhydride at 130 – 145 °C in the presence of acid catalysts (e.g., $ZnCl_2$). This 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:

$$C_2H_4 + 1/2 O_2 \rightarrow CH_3CHO \quad \Delta H = -244 \text{ kJ/mol}$$

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:

$$C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl$$
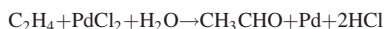
In the Wacker-Hoechst process, metallic palladium is reoxidized by $CuCl_2$, which is then regenerated with oxygen:

$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$

$$2CuCl + 1/2 O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$
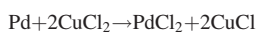
Therefore only a very small amount of $PdCl_2$ is required for the conversion of ethylene. The reaction of ethylene with palladium chloride is the rate-determining step.

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

$$[PdCl_4]^{2-} + H_2C=CH_2 \rightleftharpoons [(C_2H_4)PdCl_3]^- + Cl^-$$
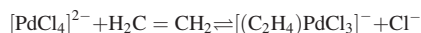
Kinetic studies of this reaction show that chloride ions have a inhibiting effect which is explained by the following substitution of a further chloride ligand by a water molecule:

$$[(C_2H_4)PdCl_3]^- + H_2O \rightleftharpoons [(C_2H_4)PdCl_2(H_2O)] + Cl^-$$
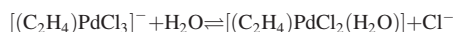
Dissociation of hydrogen ions explains the inhibiting effect of acids:

$$[(C_2H_4)PdCl_2(H_2O)] \rightleftharpoons [(C_2H_4)PdCl_2(OH)]^- + H^+$$
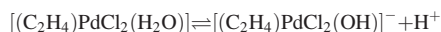
It is assumed that the hydroxyl complex has the *trans* geometry. Evidence for the *trans – cis* isomerisation of this complex was revealed by a detailed kinetic study of the reaction. π-Bonded ethylene ligands in the *trans* position weaken the metal – chlorine bonds, so that the chloro ligand can be easily substituted by a water molecule from which a hydrogen ion dissociates.

$$trans\text{-}[(C_2H_4)PdCl_2(OH)]^- + H_2O \rightleftharpoons$$
$$[(C_2H_4)PdCl(OH)_2]^- + H^+ + Cl^-$$
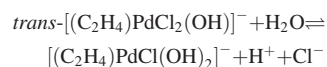
The OH^- ligand in the *trans* position is replaced by a Cl^- ion, leading to a *cis* complex:

$[(C_2H_4)PdCl(OH)_2]^- + H^+ + Cl^- \rightleftharpoons$

$\quad cis\text{-}[(C_2H_4)PdCl_2(OH)]^- + H_2O$
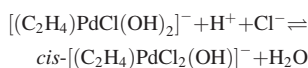
The next reaction step is the formation of a σ-bonded hydroxyethylpalladium species. This reaction has been regarded as a *cis* ligand insertion reaction in which the OH$^-$ ligand attacks the π-bonded olefin:

$cis-[(C_2H_4)PdCl_2(OH)]^- \rightleftharpoons [HOCH_2CH_2PdCl_2]^-$
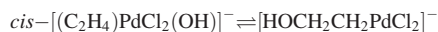
Hydride transfer to give an α-hydroxyethyl-palladium complex is followed by reductive elimination, which is the rate-determining step:

$[HOCH_2CH_2PdCl_2]^- \rightleftharpoons [CH_3CH(OH)PdCl_2]^-$

$[CH_3CH(OH)PdCl_2]^- \rightarrow CH_3CHO + Pd + H^+ + 2Cl^-$
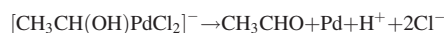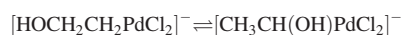
For a detailed description, see [43]. The rate of reaction can be given by the following equation [44]:

$$-\frac{d\,c_{C_2H_4}}{d\,t} = k\,\frac{c_{PdCl_4^{2-}} \cdot c_{C_2H_4}}{c_{H^+} \cdot c_{Cl^-}^2}$$

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
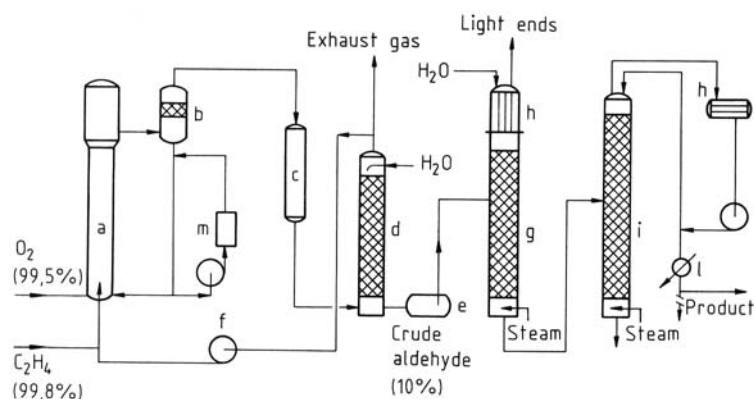

Figure 2. One-stage process
a) Reactor; b) Separating vessel; c) Cooler; d) Scrubber; e) Crude aldehyde tank; f) Cycle-gas compressor; g) Light-ends distillation; h) Condensers; i) Purification column; l) Product cooler; m) Regeneration
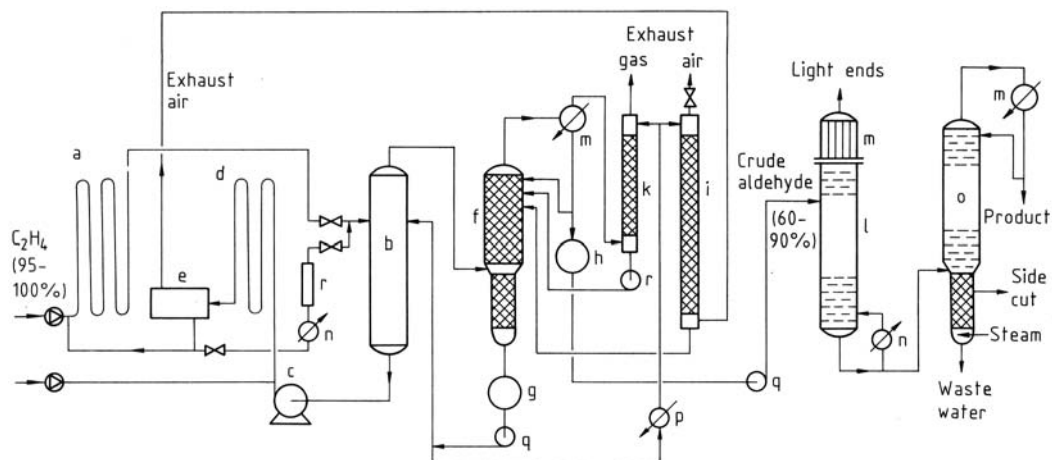
Figure 3. Two-stage process
a) Reactor; b) Flash tower; c) Catalyst pump; d) Oxidation reactor; e) Exhaust-air separator; f) Crude-aldehyde column;
g) Process-water tank; h) Crude-aldehyde container; i) Exhaust-air scrubber; k) Exhaust-gas scrubber; l) Light-ends distillation;
m) Condensers; n) Heater; o) Purification column; p) Cooler; q) Pumps; r) Regeneration

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.

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-dioxane, 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 $CuCl_2$ – $PdCl_2$ 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 Al_2O_3, SiO_2, 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 C_1 Sources

Since the increases in oil price in 1973/74 and 1977, C_1 material has gained interest as a feedstock for organic chemicals and as a substitute for petrochemicals. However, for acetaldehyde production, C_1 material seems to be of minor importance because most of the classical acetaldehyde derivatives can be made from C_1 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/H_2 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., $CoBr_2$, CoI_2) 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] ($\to$ Acetic Acid).

5. Quality and Analysis

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

Color	practically colorless
Acetaldehyde	more than 99.5 wt %
Acid (as acetic acid)	less than 0.1 wt %
Water	less than 0.02 wt %
Chlorine	less than 30 mg/kg
Dry residue	less than 10 mg/kg

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 (10^3 t) are listed in the following [56]:

Celanese Chemicals Europe GmbH, Germany	120
Eastman Chemical Company, USA	225
ECROS, SA, Spain	90
Japan Aldehyde Company Ltd., Japan	69
Jilin Chemical Industrial Company, China	180
Kyowa Yuka Company Ltd., Japan	61
Showa Denko K.K., Japan	300
Sinopec Yangzi Petrochemical Co., China	78 (400 planned)
Wacker Chemie AG, Germany	65

Table 2. Production of acetaldehyde (10^3 t) [56]

Year	USA	W. Europe	Mexico	Japan	China	Total
1990	283	603	190	384		1460
1995	111	668	271	395	400	1845
2000	155	370	113	401	400	1439
2003	142	212	57	362	500	1273

8. Polymers of Acetaldehyde

8.1. Paraldehyde

Paraldehyde, 2,4,6-trimethyl-1,3,5-trioxane [*123-63-7*], $C_6H_{12}O_3$, M_r 132.161, is a cyclic trimer of acetaldehyde:
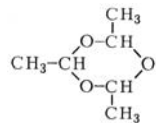
Properties. Paraldehyde is colorless and has an ethereal, penetrating odor.

|	
bp	124.35 °C
mp	12.54 °C
Critical temperature t_{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_4^{20}	0.9923
Refractive index n_D^{20}	1.4049
Viscosity at 20 °C	1.31 mPa · s
Heat of combustion at constant pressure	3405 kJ/mol
Heat capacity c_p at 25 °C	1.947 J g^{-1} K^{-1}
Entropy (l) at 25 °C	2.190 J g^{-1} K^{-1}
Free energy (l) 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, H_3PO_4, or cation exchangers. The reaction is first order. Other catalysts described in the literature are Al_2O_3, SiO_2, $ZnSO_4$, and $MgSO_4$ [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.

8.2. Metaldehyde

Metaldehyde [*9002-91-9*], $C_8H_{16}O_4$, M_r 176.214, is the cyclic tetramer of acetaldehyde:
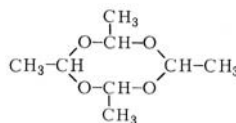
Properties. Metaldehyde forms tetragonal prisms, *mp* (closed capillary) 246.2 °C, sublimation temperature (decomp.) 115 °C, heat of combustion at constant volume 3370 kJ/mol.

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 H_2SO_4 or H_3PO_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 $CaBr_2$, 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):

$$-CH-O-CH-O-CH-O-$$
$$CH_3 \quad CH_3 \quad CH_3$$
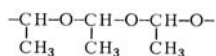
By using cationic initiators, mainly an amorphous polymer is obtained. Temperatures below −40 °C are preferred in this case. Above −30 °C, mainly paraldehyde and metaldehyde are produced. The initiator activity also depends on the solvent used. Suitable initiators include H_3PO_4 in ether and pentane, as well as HCl, HNO_3, CF_3COOH, $AlCl_3$ in ether, and particularly BF_3 in liquid ethylene [61]. Al_2O_3 and SiO_2 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 allylacetaldehyde 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 LC_{50} (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 halflife 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.
2 S. A. Miller (ed.): *Acetylene*, E. Benn, London 1965.
3 S. A. Miller (ed.): *Ethylene*, E. Benn, London 1969.
4 R. Jira in [3]: pp. 639 and 650.
5 R. Sieber in [3]: pp. 659 and 668.
6 R. Page in [3]: p. 767.
7 W. Reppe: *Chemie und Technik der Acetylen-Druck-Reaktionen*, Verlag Chemie, Weinheim 1951.
8 *Review on Manufacturing Processes of Wacker, Lonza, IG-Farben factories Hüls, Gendorf, Schkopau and Ludwigshafen, Stickstoff AG, Knapsack*, BIOS Final Report 1049, item no. 22 (1946).
9 *Report on the IG Works Hüls and Gendorf*, FIAT Final Report 855 (1946).
10 *Acetaldehyde from Acetylene*, BIOS Final Report 370.
11 *Kirk-Othmer*, 3rd ed., **1**, 97 – 112.

Specific References

12 R. C. Weast, H. J. Astle (eds.): *CRC Handbook of Chemistry and Physics*, 60th ed., CRC Press, Boca Raton, Florida 1979 – 1980.
13 D'Ans-Lax, *Taschenbuch für Chemiker und Physiker*, 3rd ed., Springer Verlag, Berlin 1964.
14 Th. F. Smith, R. F. Bonner, *Ind. Eng. Chem.* **43** (1951) 1169.
15 T. R. Das, N. R. Kuloor, *J. Indian Inst. Sci.* **50** (1968) 45.
16 P. M. Craven, J. D. Lambert, *Proc. R. Soc. (London)* 205 A (1951) 439 and 444.
17 R. W. Gallant, *Hydrocarbon Process.* **47** (1968) no. 5, 151.
18 A. K. Shaka, *Indian J. Phys.* **6** (1931) 449.
19 L. P. Filippov, *Vestn. Mosk. Univ.* **9**, no. 12, *Ser. Fiz. Mat. Estestv. Nauk.* (1954) no. 8, 45 – 48.
20 J. D. Lambert, E. N. Staines, S. D. Woods, *Proc. R. Soc. (London)* **200 A** (1950) 262.
21 *Landolt-Börnstein*, 6th ed., vol. **2**, part 4, Springer Verlag, Berlin 1961.

22 M. M. Brazhnikov, A. D. Peshchenko, O. V. Ral'ko, *Zh. Prikl. Khim (Leningrad)* **49** (1976) no. 5, 1041; *Chem. Abstr.* **85** (1976) 45 851.

23 J. D. Lambert, G. A. H. Roberts, J. S. Rowlington, V. J. Wilkinson, *Proc. R. Soc. (London)* 200 A (1960) 262.

24 P. M. Chaudhuri, R. A. Stanger, G. P. Mathur, *J. Chem. Eng. Data* **13** (1968) 9 – 11.

25 A. A. Dobrinskaya, V. G. Markovich, M. B. Neiman, *Isv. Akad. Nauk. S.S.S.R., Otd. Khim. Nauk.* 1953, 434 – 441; *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. (Engl. Transl.)* 1953, 391 – 398; *Chem. Abstr.* **49** (1955) 4378.

26 *Landholt-Börnstein*, 6th ed., vol. **2**, part 2, Springer Verlag, Berlin 1961.

27 G. O. Morrison, T. P. G. Shaw, *Trans. Electrochem. Soc.* **63** (1933) 425.

28 B. P. Mullins, *Fuel* **32** (1953) 481.

29 F. C. Mitchell, H. C. Vernon, *Chem. Met. Eng.* **44** (1937) 733.

30 K. Sennewald, *Erdöl Kohle* **12** (1959) 364.

31 *Petroleum Refiner* **40** (1961) no. 11, 308.

32 *Ullmann*, 4th ed., **9**, 6.

33 *Ullmann*, 4th ed., **7**, 374.

34 SU 287 919, 1970.

35 Heavy Minerals Co., US 2 884 460, 1955 (V.I. Komarevsky).

36 Knapsack-Griesheim, DE 1 097 969, 1954 (W. Opitz, W. Urbanski); DE 1 108 200, 1955 (W. Opitz, W. Urbanski).

37 W. L. Faith, D. B. Keyes, R. L. Clarks: *Industrial Chemicals*, 3rd ed., J. Wiley & Sons, New York 1965, p. 2.

38 Shell Development Co., US 2 883 426, 1957 (W. Brackman). Eastman Kodak Co., US 3 106 581, 1963 (S.D. Neely). Veba-Chemie, DE 1 913 311, 1969 (W. Ester, W. Hoitmann).

39 *Petroleum Refiner* **36** (1957) 249.

40 *Ullmann*, 3rd ed., **3**, 4.

41 K. Kon, T. Igarashi, *Ind. Eng. Chem.* **48** (1956) 1258.

42 Consortium für elektrochemische Industrie, DE 1 049 845, 1957 (W. Hafner, J. Smidt, R. Jira, R. Rüttinger, J. Sedlmeier). DE 1 061 767, 1957 (W. Hafner, J. Smidt, R. Jira, J. Sedlmeier); DE 1 080 994, 1957 (W. Hefner, J. Smidt, R. Jira). J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, H. Kojer, *Angew. Chem.* **71** (1959) 176; *ibid.* **74** (1962); *Angew. Chem. Int. Ed. Engl.* **1** (1962) 80; *Chem. Ind.* 1962, 54.

43 R. Jira: "Oxidations", in W. A. Herrmann (ed.): *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. **1** VCH, Weinheim 1996.

44 I. I. Moiseev, M. N. Vargaftik, Y. K. Sirkin, *Dokl. Akad. Nauk SSSR* **153** (1963) 140. P. M. Henry, *J. Am. Chem. Soc.* **86** (1964) 3246.

45 Consortium für elektrochemische Industrie, DE 1 215 677, 1964 (W. Hefner, R. Jira, J. Smidt).

46 Lummus Co., BE 668 601, 1965. W. G. Lloyd, *J. Org. Chem.* **34** (1969) 3949.

47 Erste Allgemeine Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz (Technische Anleitung zur Reinhaltung der Luft TA-Luft) vom 27.02.1986, GMBL 1986, S. 95.

48 Sicedison, FR 1 316 720, 1961 (J. Herzenberg, P. Gialtoni). British Petroleum Co., FR 1 367 963, 1963. Hoechst, US 3 067 256, 1959 (K. Fischer, K. Vester).

49 Rhône-Poulenc, EP 0 011 043, 1979 (J. Gauthier-Lafage, R. Perron). Union Carbide, US 4 235 798, 1980 (W. J. Bartley, T. P. Wilson, P. C. Ellgen). Hoechst, DE-OS 2 814 365, DE-OS 2 814 365, DE-OS 2 825 598, 1978 (H. J. Arpe, E.-J. Leupold, F. A. Wunder, H.-J. Schmidt).

50 Du Pont, US 2 457 204, 1946 (R. E. Brooks). US 3 356 734, 1963 (M. Kuraishi, S. Asano, A. Takahashi).

51 Exxon Research and Eng. Co., EP 0 027 000, 1980 (G. Doyle). Celanese Corp., US 4 201 868, 1980 (W. E. Slinkard). Union Rheinische Braunkohlen Kraftstoff, DE-OS 2913 677, 1979 (J. Korff, M. Fremery, J. Zimmermann).

52 Gulf Research & Development Co., US 4 239 704/5, 1980 (W. R. Pretzer, T. P. Kobylinsky, J. E. Bozik). British Petroleum Co., EP 0 029 723, 1980 (M.T. Barlow).

53 Rhône-Poulenc, EP 0 046 128/9, 1981 (J. Gauthier-Lafage, R. Perron). Halcon Research & Development Corp., US 4 302 611, 1981; BE 890 376, 1982 (R. V. Porcelli).

54 Halcon SD Group, FR 8 118 437/8, 1981 (D. Moy). Kuraray Co., EP 0 040 414, 1981 (S. Nakamura, M. Tamura).

55 *Ullmann*, 3rd ed., suppl. vol., p. 172.

56 B. Suresh, G. Toki: "Acetaldehyde", *Chemical Economics Handbook*, SRI International 2004.

57 Eastman Kodak Co., US 2 318 341, 1937 (B. Thompson).

58 Publicker Ind., US 2 479 559, 1947 (A. A. Dolnick *et al.*). Melle-Bezons, DE-OS 1 927 827, 1969 (M. G. Gobron, M. M. Repper).

59 T. Kawaguchi, S. Hasegawa, *Tokyo Gakugei Daigaku* **21** (1969) 63.

60 Publicker Ind., US 2 426 961, 1944 (R. S. Wilder).

61 O. Vogl, *J. Polym. Sci., Part A* **2** (1964) 4591; H. Staudinger, *Trans. Faraday Soc.* **32** (1936) 249; H. A. Rigby, C. J. Danby, C. N. Hinshelwood, *J. Chem. Soc.* 1948, 234.

62 J. T. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, T. Tatana, *J. Polym. Sci.* **36** (1959) 546. J. T. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawazaki, *Makromol. Chem.* **33** (1960) 32. Consortium für elektrochemische Industrie, DE 1 106 075, 1958 (J. Smidt, J. Sedlmeier).

63 Consortium für elektrochemische Industrie, DE 1 292 394, 1959 (J. Smidt, J. Sedlmeier).

64 Bridgestone Tire Co., FR 1 268 322 and FR 1 268 191, 1960 (J. Furukawa, T. Tsuruta, T. Saegusa, H. Fujii). J. T. Furukawa, *Makromol. Chem.* **37** (1969) 149. G. Natta, *Makromol. Chem.* **37** (1960) 156; *J. Polym. Sci.* **51** (1960) 505.

65 O. Vogl, *J. Polym. Sci., Part A* **2** (1964) 4607.

66 T. Imoto, T. Matsubara, *J. Polym. Sci.* **56** (1962) 5.

67 C. P. McCord: *Odors, Physiology and Control*, McGraw-Hill, New York 1949.

68 W. Summer: *Odour Pollution of Air Causes and Control*, Chemical and Process Engineering Series, Leonard Hill, London 1971.

69 L. Silverman, H. F. Schulte, M. W. First, *J. Ind. Hyg. Toxicol.* **28** (1946) 265.

70 V. M. Sim, R. E. Pattle, *J. Am. Med. Assoc.* **165** (1957) 1908.

71 E. Skog, *Acta Pharmacol.* **6** (1950) 299.

72 G. Obe, H. J. Ristow, *Mutat. Res.* **58** (1978) 115.

73 J. Becker, H. Desel, H. Schuster, G. F. Kahl, *Ther. Umsch.* **52** (1995) 183.

74 G. Obe, R. Jonas, S. Schmidt, *Mutat. Res.* **174** (1986) 47.

75 N. P. Singh, A. Kahn, *Mutat. Res.* **337** (1995) 9.

76 V. J. Feron, A. Kruysse, R. A. Woutersen, *Eur. J. Cancer Clin. Oncol.* **18** (1982) 13.

77 R. A. Woutersen, L. M. Appelman, A. van Garderen-Hoetmer, V. J. Feron, *Toxicology* **41** (1986) 213.

78 L. M. Appelman *et al.*, Report No. V84.382/140327, CIVO Institutes TNO, NL-3700AJ Zeist, The Netherlands, 1985.

79 *1997 TLVs and BEIs*. American Conference of Governmental Industrial Hygienists Inc., Cincinnati, Ohio 1997.

80 DFG Deutsche Forschungsgemeinschaft: *Occupational Toxicants: Critical Data for MAK Values and Classification of Carcinogens*, vol. **3**, Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, VCH Verlagsgesellschaft, Weinheim 1992.

81 K. J. Freundt, *Naunyn-Schmiedeberg's Arch. Exp. Pathol. Pharmakol.* **260** (1968) 111; *Beitr. Gerichtl. Med.* **27** (1970) 368.

82 O. R. Klimmer: *Pflanzenschutz- und Schädlingsbekämpfungsmittel, Abriß einer Toxikologie und Therapie von Vergiftungen*, Hundt-Verlag, Hattingen 1972.

Further Reading

J. G. Calvert, R. G. Derwent, J. J. Orlando, G. S. Tyndall, T. J. Wallington: *Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford University Press, New York, NY 2008.

G. P. Chiusoli, P. M. Maitlis (eds.): *Metal-Catalysis in Industrial Organic Processes*, Royal Society of Chemistry, Cambridge, UK 2006.

H. J. Hagemeyer: *Acetaldehyde, Kirk Othmer Encyclopedia of Chemical Technology*, 5th ed., vol. 1, p. 99–114, John Wiley & Sons, Hoboken, NJ, 2004, online: DOI: 10.1002/0471238961.0103052008010705.a01.pub2 (November 2002)

J. Hagen: *Industrial Catalysis*, 2nd ed., Wiley-VCH, Weinheim 2006.

S. Minteer (ed.): *Alcoholic Fuels*, CRC/Taylor & Francis, Boca Raton, FL 2006.

M. V. Moreno-Arribas, M. C. Polo (eds.): *Wine Chemistry and Biochemistry*, Springer, New York, NY 2009.

C. D. Papaspyrides, S. N. Vouyiouka (eds.): *Solid State Polymerization*, Wiley, Hoboken, NJ 2009.