ACETALDEHYDE

1. Introduction

Acetaldehyde [75-07-0] (ethanal), CH_3CHO, was first prepared by Scheele in 1774, by the action of manganese dioxide and sulfuric acid on ethanol. The structure of acetaldehyde was established in 1835 by Liebig from a pure sample prepared by oxidizing ethyl alcohol with chromic acid. Liebig named the compound "aldehyde" from the Latin words translated as al(cohol) dehyd(rogenated). The formation of acetaldehyde by the addition of water to acetylene was observed by Kutscherow in 1881.

Acetaldehyde, first used extensively during World War I as a starting material for making acetone [67-64-1] from acetic acid [64-19-7], is an important intermediate in the production of acetic acid, acetic anhydride [108-24-7], ethyl acetate [141-78-6], peracetic acid [79-21-0], pentaerythritol [115-77-5], chloral [302-17-0], glyoxal [107-22-2], alkylamines and pyridines. Commercial processes for acetaldehyde production include the oxidation or dehydrogenation of ethanol, the addition of water to acetylene, the partial oxidation of hydrocarbons, and the direct oxidation of ethylene [74-85-1].

Acetaldehyde is a product of most hydrocarbon oxidations. It is an intermediate product in the respiration of higher plants and occurs in trace amounts in all ripe fruits that have a tart taste before ripening. The aldehyde content of volatiles has been suggested as a chemical index of ripening during cold storage of apples. Acetaldehyde is also an intermediate product of fermentation (qv), but it is reduced almost immediately to ethanol. It may form in wine (qv) and other alcoholic beverages after exposure to air imparting an unpleasant taste; the aldehyde reacts to form diethyl acetal [105-57-7] and ethyl acetate [141-78-6]. Acetaldehyde is an intermediate product in the decomposition of sugars in the it body and hence occurs in trace quantities in blood.

2. Physical Properties

Acetaldehyde is a colorless, mobile liquid having a pungent, suffocating odor that is somewhat fruity and quite pleasant in dilute concentrations. Its physical

Table 1. **Physical Properties of Acetaldehyde**

Properties	Values
formula weight	44.053
melting point, °C	−123.5
boiling point at 101.3 kPa[a] (1 atm), °C	20.16
density, g/mL	
d_4^{0}	0.8045
d_4^{11}	0.7901
d_4^{15}	0.7846
d_4^{20}	0.7780
coefficient of expansion per °C (0–30°C)	0.00169
refractive index, n_D^{20}	1.33113
vapor density (air = 1)	1.52
surface tension at 20°C, mN/m (= dyn/cm)	21.2
absolute viscosity at 15°C, mPa·s (= cP)	0.02456
specific heat at 0°C, J/(g·K)[b]	
15°C	2.18
25°C	1.41
$\alpha = C_p/C_v$ at 30°C and 101.3 kPa[a] (1 atm)	1.145
latent heat of fusion, kJ/mol[b]	3.24
latent heat of vaporization, kJ/mol[b]	25.71
heat of solution in water, kJ/mol[b]	
at 0°C	−8.20
at 25°C	−6.82
heat of combustion of liquid at constant pressure, kJ/mol[b]	12867.9
heat of formation at 273 K, kJ/mol[b]	−165.48
free energy of formation at 273 K, kJ/mol[b]	−136.40
critical temperature, °C	181.5
critical pressure, MPa[c]	6.40
dipole moment, C·m[d]	8.97×10^{-30}
ionization potential, eV	10.50
dissociation constant at 0°C, K_a	0.7×10^{-14}
flash point, closed cup, °C	−38
ignition temperature in air, °C	165
explosive limits of mixtures with air, vol % acetaldehyde	4.5–60.5

[a] To convert kPa to psi, multiply by 0.14503.
[b] To convert J to cal, divide by 4.187.
[c] To convert MPa to psi, multiply by 145.
[d] To convert C·m to debyes, multiply by 2.998×10^{29}.

properties are given in Table 1; the vapor pressure of acetaldehyde and its aqueous solutions appear in Tables 2 and 3, respectively; and the solubilities of acetylene, carbon dioxide and nitrogen in liquid acetaldehyde are given in Table 4. Acetaldehyde is miscible in all proportions with water and most common organic solvents, eg, acetone, benzene, ethyl alcohol, ethyl ether, gasoline, paraldehyde, toluene, xylenes, turpentine, and acetic acid. The freezing points of aqueous solutions of acetaldehyde are 4.8 wt %, −2.5°C; 13.5 wt %, −7.8°C; and 31.0 wt % −23.0°C.

Given in the literature are: vapor pressure data for acetaldehyde and its aqueous solutions (1–3); vapor–liquid equilibria data for acetaldehyde–ethylene oxide (1), acetaldehyde–methanol (4), sulfur dioxide–acetaldehyde–water (5), acetaldehyde–water–methanol (6); the azeotropes of acetaldehyde–butane and

Table 2. **Vapor Pressure of Acetaldehyde**

Temperature, °C	Vapor pressure, kPa[a]	Temperature, °C	Vapor pressure, kPa[a]
−50	2.5	20	100.6
−20	16.4	20.16	101.3
0	44.0	30	145.2
5	54.8	50	279.4
10	67.7	70	492.6
15	82.9	100	1,014

[a] To convert kPa to mm Hg, multiply by 7.5.

Table 3. **Vapor Pressure of Aqueous Solutions of Acetaldehyde**

Temperature, °C	Mol %	Total vapor pressure, kPa[a]
10	4.9	9.9
10	10.5	18.6
10	46.6	48.4
20	5.4	16.7
20	12.9	39.3
20	21.8	57.7

[a] To convert kPa to mm Hg, multiply by 7.5.

acetaldehyde–ethyl ether (7); solubility data for acetaldehyde–water–methane (8), acetaldehyde–methane (9); densities and refractive indexes of acetaldehyde for temperatures 0–20°C (2); compressibility and viscosity at high pressure (10); thermodynamic data (11–13); pressure-enthalpy diagram for acetaldehyde (14); specific gravities of acetaldehyde–paraldehyde and acetaldehyde–acetaldol mixtures at 20/20°C vs composition (7); boiling point vs composition of acetaldehyde–water at 101.3 kPa (1 atm) and integral heat of solution of acetaldehyde in water at 11°C (7).

Table 4. **Solubility of Gases in Liquid Acetaldehyde at Atmospheric Pressure**

	Volume of gas (STP) dissolved in 1 volume acetaldehyde		
Temperature, °C	Acetylene	Carbon dioxide	Nitrogen
−16	54		
−6	27	11	
0	17	6.6	
12	7.3	14.5	0.15
16	5	1.5	
20	3		

3. Chemical Properties

The limits and products of the various combustion zones for acetaldehyde–oxygen and acetaldehyde–air have been described (15–18); the effect of pressure on the explosive limits of acetaldehyde–air mixtures has been investigated (19). In a study of the spontaneous ignition of fuels injected into hot air streams, it was found that acetaldehyde was the least ignitable of the aldehydes examined (20,21). The influence of surfaces on the ignition and detonation of fuels containing acetaldehyde has been reported (22,23). Ignition data have been published for the systems acetaldehyde–oxygen–peroxyacetic acid–acetic acid (24), acetaldehyde–oxygen–peroxyacetic acid (25), and ethylene oxide–air–acetaldehyde (26).

Acetaldehyde is a highly reactive compound exhibiting the general reactivity ofaldehydes (qv). Acetaldehyde undergoes numerous condensation, addition, and polymerization reactions; under suitable conditions, the oxygen or any of the hydrogens can be replaced.

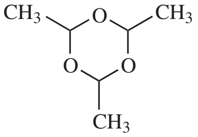
3.1. Decomposition. Acetaldehyde decomposes at temperatures above 400°C, forming principally methane and carbon monoxide. The activation energy of the pyrolysis reaction is 97.7 kJ/mol (408.8 kcal/mol) (27). There have been many investigations of the photolytic and radical-induced decomposition of acetaldehyde and deuterated acetaldehyde (28–30).

3.2. The Hydrate and Enol Form. In aqueous solutions, acetaldehyde exists in equilibrium with the acetaldehyde hydrate [4433-56-1], ($CH_3CH(OH)_2$). The degree of hydration can be computed from an equation derived by Bell and Clunie (31). Hydration, the mean heat of which is -21.34 kJ/mol (-89.29 kcal/mol), has been attributed to hyperconjugation (32). The enol form, vinyl alcohol [557-75-5] ($CH_2{=}CHOH$) exists in equilibrium with acetaldehyde to the extent of approximately one molecule per 30,000. Acetaldehyde enol has been acetylated with ketene [463-51-4] to form vinyl acetate [108-05-4] (33).

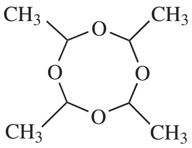
3.3. Oxidation. Acetaldehyde is readily oxidized with oxygen or air to acetic acid, acetic anhydride, and peracetic acid (see ACETIC ACID AND DERIVATIVES). The principal product depends on the reaction conditions. Acetic acid [64-19-7] may be produced commercially by the liquid-phase oxidation of acetaldehyde at 65°C using cobalt or manganese acetate dissolved in acetic acid as a catalyst (34). Liquid-phase oxidation in the presence of mixed acetates of copper and cobalt yields acetic anhydride [108-24-7] (35). Peroxyacetic acid or a perester is believed to be the precursor in both syntheses. There are two commercial processes for the production of peracetic acid [79-21-0]. Low temperature oxidation of acetaldehyde in the presence of metal salts, ultraviolet irradiation, or ozone yields acetaldehyde monoperacetate, which can be decomposed to peracetic acid and acetaldehyde (36). Peracetic acid can also be formed directly by liquid-phase oxidation at 5–50°C with a cobalt salt catalyst (37) (see PEROXIDES AND PEROXY COMPOUNDS). Nitric acid oxidation of acetaldehyde yields glyoxal [107-22-2] (38,39). Oxidations of *p*-xylene to terephthalic acid [100-21-0] and of ethanol to acetic acid are activated by acetaldehyde (40,41).

3.4. Reduction. Acetaldehyde is readily reduced to ethanol (qv). Suitable catalysts for vapor-phase hydrogenation of acetaldehyde are supported nickel (42) and copper oxide (43). The kinetics of the hydrogenation of acetaldehyde over a commercial nickel catalyst have been studied (44).

3.5. Polymerization. Paraldehyde, 2,4,6-trimethyl-1,3-5-trioxane [123-63-7], a cyclic trimer of acetaldehyde, is formed when a mineral acid, such as sulfuric, phosphoric, or hydrochloric acid, is added to acetaldehyde (45). Paraldehyde can also be formed continuously by feeding liquid acetaldehyde at 15–20°C over an acid ion-exchange resin (46). Depolymerization of paraldehyde occurs in the presence of acid catalysts (47); after neutralization with sodium acetate, acetaldehyde and paraldehyde are recovered by distillation. Paraldehyde is a colorless liquid, boiling at 125.35°C at 101 kPa (1 atm).



paraldehyde



metaldehyde

Metaldehyde [9002-91-9], a cyclic tetramer of acetaldehyde, is formed at temperatures below 0°C in the presence of dry hydrogen chloride or pyridine–hydrogen bromide. The metaldehyde crystallizes from solution and is separated from the paraldehyde by filtration (48). Metaldehyde melts in a sealed tube at 246.2°C and sublimes at 115°C with partial depolymerization.

Polyacetaldehyde, a rubbery polymer with an acetal structure, was first discovered in 1936 (49,50). More recently, it has been shown that a white, nontacky, and highly elastic polymer can be formed by cationic polymerization using BF_3 in liquid ethylene (51). At temperatures below −75°C using anionic initiators, such as metal alkyls in a hydrocarbon solvent, a crystalline, isotactic polymer is obtained (52). This polymer also has an acetal [poly(oxymethylene)] structure. Molecular weights in the range of 800,000–3,000,000 have been reported. Polyacetaldehyde is unstable and depolymerizes in a few days to acetaldehyde. The methods used for stabilizing polyformaldehyde have not been successful with polyacetaldehyde and the polymer has no practical significance (see ACETAL RESINS).

3.6. Reactions with Aldehydes and Ketones. The base-catalyzed self-addition of acetaldehyde leads to formation of the dimer, acetaldol [107-89-1], which can be hydrogenated to form 1,3-butanediol or dehydrated to form crotonaldehyde [4170-30-3]. Crotonaldehyde (qv) can also be made directly by the vapor-phase condensation of acetaldehyde over a catalyst (53).

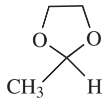
Acetaldehyde forms aldols with other carbonyl compounds containing active hydrogen atoms. Kinetic studies of the aldol condensation of acetaldehyde and deuterated acetaldehydes have shown that only the hydrogen atoms bound to the carbon adjacent to the CHO group take part in the condensation reactions and hydrogen exchange (54,55). A hexyl alcohol, 2-ethyl-1-butanol [97-95-0], is produced industrially by the condensation of acetaldehyde and butyraldehyde in dilute caustic solution followed by hydrogenation of the enal intermediate (see ALCOHOLS, HIGHER ALIPHATIC). Condensation of acetaldehyde in the presence of dimethylamine hydrochloride yields polyenals which can be hydrogenated to a mixture of alcohols containing from 4 to 22 carbon atoms (56).

The base-catalyzed reaction of acetaldehyde with excess formaldehyde is the commercial route to pentaerythritol [115-77-5]. The aldol condensation of three moles of formaldehyde with one mole of acetaldehyde is followed by a crossed Cannizzaro reaction between pentaerythrose, the intermediate product, and formaldehyde to give pentaerythritol (57). The process proceeds to completion without isolation of the intermediate. Pentaerythrose [3818-32-4] has also been made by condensing acetaldehyde and formaldehyde at 45°C using magnesium oxide as a catalyst (58). The vapor-phase reaction of acetaldehyde and formaldehyde at 475°C over a catalyst composed of lanthanum oxide on silica gel gives acrolein [107-02-8] (59).

Ethyl acetate [141-78-6] is produced commercially by the Tischenko condensation of acetaldehyde using an aluminum ethoxide catalyst (60). The Tischenko reaction of acetaldehyde with isobutyraldehyde [78-84-2] yields a mixture of ethyl acetate, isobutyl acetate [110-19-0], and isobutyl isobutyrate [97-85-8] (61).

3.7. Reactions with Ammonia and Amines. Acetaldehyde readily adds ammonia to form acetaldehyde–ammonia. Diethylamine [109-89-7] is obtained when acetaldehyde is added to a saturated aqueous or alcoholic solution of ammonia and the mixture is heated to 50–75°C in the presence of a nickel catalyst and hydrogen at 1.2 MPa (12 atm). Pyridine [110-86-1] and pyridine derivatives are made from paraldehyde and aqueous ammonia in the presence of a catalyst at elevated temperatures (62); acetaldehyde may also be used but the yields of pyridine are generally lower than when paraldehyde is the starting material. The vapor-phase reaction of formaldehyde, acetaldehyde, and ammonia at 360°C over oxide catalyst was studied; a 49% yield of pyridine and picolines was obtained using an activated silica–alumina catalyst (63). Brown polymers result when acetaldehyde reacts with ammonia or amines at a pH of 6–7 and temperature of 3–25°C (64). Primary amines and acetaldehyde condense to give Schiff bases: $CH_3CH{=}NR$. The Schiff base reverts to the starting materials in the presence of acids.

3.8. Reactions with Alcohols, Mercaptans, and Phenols. Alcohols add readily to acetaldehyde in the presence of trace quantities of mineral acid to form acetals; eg, ethanol and acetaldehyde form diethyl acetal [105-57-7] (65). Similarly, cyclic acetals are formed by reactions with glycols and other polyhydroxy compounds; eg, ethylene glycol [107-21-1] and acetaldehyde give 2-methyl-1,3-dioxolane [497-26-7] (66):



Mercaptals, $CH_3CH(SR)_2$, are formed in a like manner by the addition of mercaptans. The formation of acetals by noncatalytic vapor-phase reactions of acetaldehyde and various alcohols at 35°C has been reported (67). Butadiene [106-99-0] can be made by the reaction of acetaldehyde and ethyl alcohol at temperatures above 300°C over a tantala–silica catalyst (68). Aldol and crotonaldehyde are believed to be intermediates. Butyl acetate [123-86-4] has been prepared by the catalytic reaction of acetaldehyde with 1-butanol [71-36-3] at 300°C (69).

Reaction of one mole of acetaldehyde and excess phenol in the presence of a mineral acid catalyst gives 1,1-bis(*p*-hydroxyphenyl)ethane [2081-08-5]; acid catalysts, acetaldehyde, and three moles or less of phenol yield soluble resins. Hardenable resins are difficult to produce by alkaline condensation of acetaldehyde and phenol because the acetaldehyde tends to undergo aldol condensation and self-resinification (see PHENOLIC RESINS).

3.9. Reactions with Halogens and Halogen Compounds. Halogens readily replace the hydrogen atoms of the acetaldehyde's methyl group: chlorine reacts with acetaldehyde or paraldehyde at room temperature to give chloroacetaldehyde [107-20-0]; increasing the temperature to 70–80°C gives dichloroacetaldehyde [79-02-7]; and at a temperature of 80–90°C chloral [302-17-0] is formed (70). Catalytic chlorination using antimony powder or aluminum chloride–ferric chloride has also been described (71). Bromal [115-17-3] is formed by an analogous series of reactions (72). It has been postulated that acetyl bromide [506-96-7] is an intermediate in the bromination of acetaldehyde in aqueous ethanol (73). Acetyl chloride [75-36-5] has been prepared by the gas-phase reaction of acetaldehyde and chlorine (74).

Acetaldehyde reacts with phosphorus pentachloride to produce 1,1-dichloroethane [75-34-3] and with hypochlorite and hypoiodite to yield chloroform [67-66-3] and iodoform [75-47-8], respectively. Phosgene [75-44-5] is produced by the reaction of carbon tetrachloride with acetaldehyde in the presence of anhydrous aluminum chloride (75). Chloroform reacts with acetaldehyde in the presence of potassium hydroxide and sodium amide to form 1,1,1-trichloro-2-propanol [7789-89-1] (76).

3.10. Miscellaneous Reactions. Sodium bisulfite adds to acetaldehyde to form a white crystalline addition compound, insoluble in ethyl alcohol and ether. This bisulfite addition compound is frequently used to isolate and purify acetaldehyde, which may be regenerated with dilute acid. Hydrocyanic acid adds to acetaldehyde in the presence of an alkali catalyst to form cyanohydrin; the cyanohydrin may also be prepared from sodium cyanide and the bisulfite addition compound. Acrylonitrile [107-13-1] (qv) can be made from acetaldehyde and hydrocyanic acid by heating the cyanohydrin that is formed to 600–700°C (77). Alanine [302-72-7] can be prepared by the reaction of an ammonium salt and an alkali metal cyanide with acetaldehyde; this is a general method for the preparation of α-amino acids called the Strecker amino acids synthesis. Grignard reagents add readily to acetaldehyde, the final product being a secondary alcohol. Thioacetaldehyde [2765-04-0] is formed by reaction of acetaldehyde with hydrogen sulfide; thioacetaldehyde polymerizes readily to the trimer.

Acetic anhydride adds to acetaldehyde in the presence of dilute acid to form ethylidene diacetate [542-10-9]; boron fluoride also catalyzes the reaction (78).

Ethylidene diacetate decomposes to the anhydride and aldehyde at temperatures of 220–268°C and initial pressures of 14.6–21.3 kPa (110–160 mm Hg) (79), or upon heating to 150°C in the presence of a zinc chloride catalyst (80). Acetone (qv) [67-64-1] has been prepared in 90% yield by heating an aqueous solution of acetaldehyde to 410°C in the presence of a catalyst (81). Active methylene groups condense acetaldehyde. The reaction of isobutylene [115-11-7] and aqueous solutions of acetaldehyde in the presence of 1–2% sulfuric acid yields alkyl-*m*-dioxanes; 2,4,4,6-tetramethyl-*m*-dioxane [5182-37-6] is produced in yields up to 90% (82).

4. Manufacture

Since 1960, the liquid-phase oxidation of ethylene has been the process of choice for the manufacture of acetaldehyde. There is, however, still some commercial production by the partial oxidation of ethyl alcohol and hydration of acetylene. The economics of the various processes are strongly dependent on the prices of the feedstocks. Acetaldehyde is also formed as a coproduct in the high temperature oxidation of butane. A more recently developed rhodium catalyzed process produces acetaldehyde from synthesis gas as a coproduct with ethyl alcohol and acetic acid (83–94).

4.1. Oxidation of Ethylene. In 1894 F. C. Phillips observed the reaction of ethylene [74-85-1] in an aqueous palladium(II) chloride solution to form acetaldehyde.

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2\ HCl$$

The direct liquid phase oxidation of ethylene was developed in 1957–1959 by Wacker-Chemie and Farbwerke Hoechst in which the catalyst is an aqueous solution of $PdCl_2$ and $CuCl_2$ (86).

Studies of the reaction mechanism of the catalytic oxidation suggest that a *cis*-hydroxyethylene–palladium π-complex is formed initially, followed by an intramolecular exchange of hydrogen and palladium to give a *gem*-hydroxyethylpalladium species that leads to acetaldehyde and metallic palladium (88–90).

The metallic palladium is reoxidized to $PdCl_2$ by the $CuCl_2$ and the resultant cuprous chloride is then reoxidized by oxygen or air as shown.

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

$$2\ CuCl + 1/2\ O_2 + 2\ HCl \longrightarrow 2\ CuCl_2 + H_2O$$

Thus ethylene is oxidized continuously through a series of oxidation–reduction reactions (87,88). The overall reaction is

$$C_2H_4 + 1/2\ \ O_2 \longrightarrow CH_3CHO \quad \Delta H = 427\ \text{kJ}\ (102\ \text{kcal})$$

There are two variations for this commercial production route: the two-stage process developed by Wacker-Chemie and the one-stage process developed

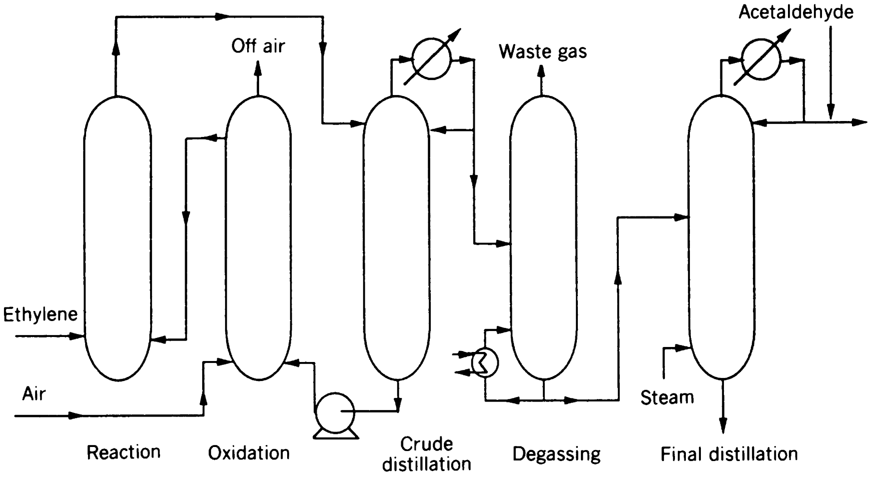


Fig. 1. The two-stage acetaldehyde process.

by Farbwerke Hoechst (91–92). In the two-stage process shown in Figure 1, ethylene is almost completely oxidized by air to acetaldehyde in one pass in a tubular plug-flow reactor made of titanium (93,94). The reaction is conducted at 125–130°C and 1.13 MPa (150 psig) using the palladium and cupric chloride catalysts. Acetaldehyde produced in the first reactor is removed from the reaction loop by adiabatic flashing in a tower. The flash step also removes the heat of reaction. The catalyst solution is recycled from the flash-tower base to the second stage (or oxidation reactor) where the cuprous salt is oxidized to the cupric state with air. The high pressure off-gas from the oxidation reactor, mostly nitrogen, is separated from the liquid catalyst solution and scrubbed to remove acetaldehyde before venting. A small portion of the catalyst stream is heated in the catalyst regenerator to destroy any undesirable copper oxalate. The flasher overhead is fed to a distillation system where water is removed for recycle to the reactor system and organic impurities, including chlorinated aldehydes, are separated from the purified acetaldehyde product. Synthesis techniques purported to reduce the quantity of chlorinated by-products generated have been patented (95).

In the one-stage process (Fig. 2), ethylene, oxygen, and recycle gas are directed to a vertical reactor for contact with the catalyst solution under slight pressure. The water evaporated during the reaction absorbs the heat evolved, and make-up water is fed as necessary to maintain the desired catalyst concentration. The gases are water-scrubbed and the resulting acetaldehyde solution is fed to a distillation column. The tail-gas from the scrubber is recycled to the reactor. Inert materials are eliminated from the recycle gas in a bleed-stream which flows to an auxiliary reactor for additional ethylene conversion.

This oxidation process for olefins has been exploited commercially principally for the production of acetaldehyde, but the reaction can also be applied to the production of acetone from propylene and methyl ethyl ketone [78-93-3] from

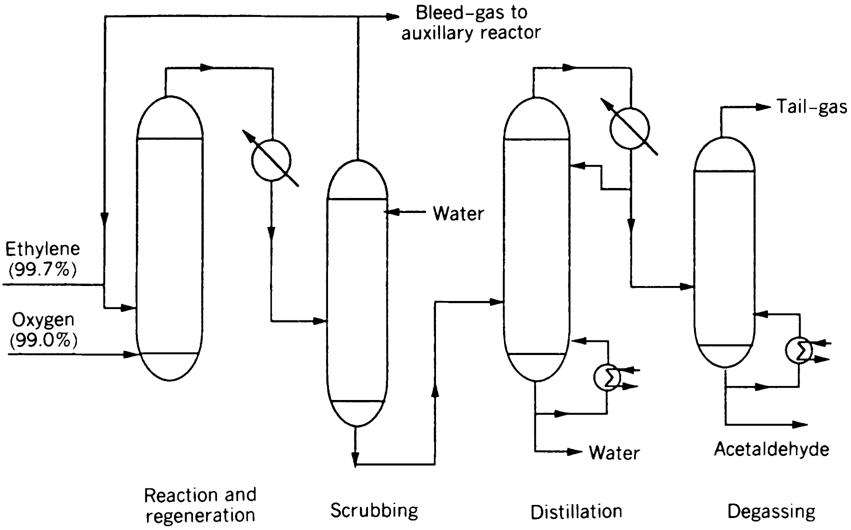


Fig. 2. The one-stage acetaldehyde process.

butenes (87,88). Careful control of the potential of the catalyst with the oxygen stream in the regenerator minimizes the formation of chloroketones (94). Vinyl acetate can also be produced commercially by a variation of this reaction (96,97). A method for preparing acetaldehyde from ethylene and oxygen has been patented (98). It is an improved process for the separation of catalyst.

4.2. From Ethyl Alcohol. Some acetaldehyde is produced commercially by the catalytic oxidation of ethyl alcohol. The oxidation is carried out by passing alcohol vapors and preheated air over a silver catalyst at 480°C (99).

$$CH_3CH_2OH + 1/2\ O_2 \longrightarrow CH_3CHO + H_2O$$

$$\Delta H = -242\ \text{kJ/mol}\ (-57.84\ \text{kcal/mol})$$

With a multitubular reactor, conversions of 74–82% per pass can be obtained while generating steam to be used elsewhere in the process (100).

4.3. From Acetylene. Although acetaldehyde has been produced commercially by the hydration of acetylene since 1916, this procedure has been almost completely replaced by the direct oxidation of ethylene. In the hydration process, high purity acetylene under a pressure of 103.4 kPa (15 psi) is passed into a vertical reactor containing a mercury catalyst dissolved in 18–25% sulfuric acid at 70–90°C (see ACETYLENE-DERIVED CHEMICALS).

$$HC{\equiv}CH + H_2O \xrightarrow[H_2SO_4(70-90^\circ C)]{Hg^{2+}} CH_3CHO$$

Fresh catalyst is fed to the reactor periodically; the catalyst may be added in the mercurous form but the catalytic species has been shown to be a mercuric ion complex (101). The excess acetylene sweeps out the dissolved acetaldehyde, which is condensed by water and refrigerated brine and then scrubbed with water; this crude acetaldehyde is purified by distillation; the unreacted acetylene is recycled. The catalytic mercuric ion is reduced to catalytically inactive mercurous sulfate and metallic mercury. Sludge, consisting of reduced catalyst and tars, is drained from the reactor at intervals and resulfated. The rate of catalyst depletion can be reduced by adding ferric or other suitable ions to the reaction solution. These ions reoxidize the mercurous ion to the mercuric ion; consequently, the quantity of sludge which must be recovered is reduced (80,102). In one variation, acetylene is completely hydrated with water in a single operation at 68–73°C using the mercuric–iron salt catalyst. The acetaldehyde is partially removed by vacuum distillation and the mother liquor recycled to the reactor. The aldehyde vapors are cooled to about 35°C, compressed to 253 kPa (2.5 atm), and condensed. It is claimed that this combination of vacuum and pressure operations substantially reduces heating and refrigeration costs (103).

4.4. From Synthesis Gas. A rhodium-catalyzed process capable of converting synthesis gas directly into acetaldehyde in a single step has been reported (83,84).

$$CO + H_2 \longrightarrow CH_3CHO + \text{other products}$$

This process comprises passing synthesis gas over 5% rhodium on SiO_2 at 300°C and 2.0 MPa (20 atm). Principal coproducts are acetaldehyde, 24%; acetic acid, 20%; and ethanol, 16%. Although interest in new routes to acetaldehyde has fallen as a result of the reduced demand for this chemical, one possible new route to both acetaldehyde and ethanol is the reductive carbonylation of methanol (85).

$$CH_3OH + CO + H_2 \longrightarrow CH_3CHO + H_2O$$

The catalyst of choice is cobalt iodide with various promotors from Group 15 elements. The process is run at 140–200°C, 28–41 MPa (4,000–6,000 psi), and gives an 88% conversion with 90% selectively to acetaldehyde. Neither of these acetaldehyde syntheses have been commercialized.

4.5. Other. A method for preparing acetaldehyde from acetic aid has been patented. The object of this preparation is to provide a method of producing acetylene that avoids the dangers associated with mercury and acetylene and the handling problems associated with reacting ethylene and oxygen, and for easy recovery of acetaldehyde (104).

5. Economic Aspects

The production pattern for acetaldehyde has undergone significant changes since the principal industrial routes to acetaldehyde were hydration of acetylene and oxidation of ethyl alcohol. First, increasing acetylene costs made this feedstock economically unattractive. Then the two aldehyde Wacker-Hoechst GmbH processes for the liquid-phase oxidation of ethylene to acetaldehyde began commercial operation. By 1968 more acetaldehyde was produced by the direct oxidation of ethylene using the Wacker process than from ethanol. Union Carbide discontinued its annual production of 90,700 t of acetaldehyde from ethanol in late 1977 (105). The percentage of ethanol consumed for acetaldehyde in the United States dropped from 20% in 1971 to zero in 1984.

Demand for acetaldehyde has decreased primarily as a result of less consumption for acetic acid production. At year-end 2000, all North American manufacture of acetic acid from acetaldehyde had been discontinued. Only China has increased capacity. Western Europe and China are the largest consumers of acetaldehyde. Since 1995 360 X 10^3 t capacity has been shut down in Western Europe and Mexico. More plant closures are expected (106).

6. Specifications, Analytical and Test Methods

Commercial acetaldehyde has the following typical specifications: assay, 99% min; color, water-white; acidity, 0.5% max (acetic acid); specific gravity, 0.790 at 20°C; bp, 20.8°C at 101.3 kPa (1 atm). It is shipped in steel drums and tank cars bearing the ICC red label. In the liquid state, it is noncorrosive to most metals; however, acetaldehyde oxidizes readily, particularly in the vapor state, to acetic acid. Precautions to be observed in the handling of acetaldehyde have been published (107).

Analytical methods based on many of the reactions common to aldehydes have been developed for acetaldehyde determination. In the absence of other aldehydes, it can be detected by the formation of a mirror from an alkaline silver nitrate solution (Tollens' reagent) and by the reduction of Fehling's solution. It can be determined quantitatively by fuchsin–sulfur dioxide solution (Schiff's reagent), or by reaction with sodium bisulfite, the excess bisulfite being estimated iodometrically. Acetaldehyde present in mixtures with other carbonyl compounds, such as organic acids, can be determined by paper chromatography of 2,4-dinitrophenylhydrazones (108), polarographic analysis either of the untreated mixture (109) or of the semicarbazones (110), the color reaction with thymol blue on silica gel (detector tube method) (111), mercurimetric oxidation (112), argentometric titration (113), microscopic (114) and spectrophotometric methods (115), and gas–liquid chromatographic analysis (116). However, gas–liquid chromatographic techniques have superseded most chemical tests for routine analyses.

Acetaldehyde can be isolated and identified by the characteristic melting points of the crystalline compounds formed with hydrazines, semicarbazides, etc; these derivatives of aldehydes can be separated by paper and column chromatography (108,117). Acetaldehyde has been separated quantitatively from other carbonyl compounds on an ion-exchange resin in the bisulfite form; the aldehyde is then eluted from the column with a solution of sodium chloride (118). In larger quantities, acetaldehyde may be isolated by passing the vapor into ether, then saturating with dry ammonia; acetaldehyde–ammonia crystallizes from the solution. Reactions with bisulfite, hydrazines, oximes, semicarbazides, and 5,5-dimethyl-1,3-cyclohexanedione [126-81-8] (dimedone) have also been used to isolate acetaldehyde from various solutions.

7. Health and Safety Factors

Acetaldehyde appears to paralyze respiratory muscles, causing panic. It has a general narcotic action which prevents coughing, causes irritation of the eyes and mucous membranes, and accelerates heart action. When breathed in high concentration, it causes headache and sore throat. Carbon dioxide solutions in acetaldehyde are particularly pernicious because the acetaldehyde odor is weakened by the carbon dioxide. Prolonged exposure causes a decrease of both red and white blood cells; there is also a sustained rise in blood pressure (119–121). IARC rates acetaldehyde as 2B (possible carcinogen to humans, NTP rates acetaldehyde as reasonably anticipated to be a human carcinogen. OSHA PEL = 200 ppm (122). In normal industrial operations there is no health hazard in handling acetaldehyde provided normal precautions are taken. Mixtures of acetaldehyde vapor and air are flammable; they are explosive if the concentrations of aldehyde and oxygen rise above 4 and 9%, respectively. Reference 107 discusses handling precautions.

8. Uses

Acetaldehyde production is linked with the demand for acetic acid, acetic anhydride, cellulose acetate, vinyl acetate resins, acetate esters, pentaerythritol, synthetic pyridine derivatives, terephthalic acid, and peracetic acid. In 1976 acetic acid production represented 60% of the acetaldehyde demand. That demand has diminished as a result of the rising cost of ethylene as feedstock and methanol carbonylation as the preferred route to acetic acid (qv).

Synthetic pyridine derivatives, peracetic acid, acetate esters by the Tischenko route, and pentaerythritol account for most (106) of acetaldehyde demand. This sector appears secure, but no new significant applications are expected for 2001–2005.

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