

2.1 PHYSICAL PROPERTIES:

Acetaldehyde is a colorless, mobile liquid having a pungent suffocating odor that is somewhat fruity and pleasant in dilute concentrations. Some physical properties of acetaldehyde are given in Table 1.1.

The freezing points of aqueous solutions of acetaldehyde are as follows:

4.8 wt %, -2.5⁰C; 13.5 wt %, - 7.8⁰ C, and 31.0 wt %, - 23.0⁰ C.

Acetaldehyde is miscible in all proportions with water and most common organic solvents: acetone, benzene, ethyl alcohol, ethyl ether, gasoline, paraldehyde, toluene, xylenes, turpentine, and acetic acid.

Table 2.1. PHYSICAL PROPERTIES OF ACETALDEHYDE

Properties	Values
Formula weight	44.053
Melting point	-123.5
Boiling point at 101.3 kPa (1 atm), °C	20.16
Density, d ₄ [°]	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 _{D20}	1.33113
Vapor density (air = 1)	1.52
Surface tension at 20 °C,mN/ma	21.2
Absolute viscosity at 15 °CmPa.s b	0.02456
Specific heat at 0 °C,J/(g.K)	2.18
At 25 °C c	1.41
$\alpha = C_p / C_v$ at 30 °Cand 101.3 kPa c	1.145

Latent heat of fusion, kJ/mol c	3.24
Latent heat of vaporization, kJ/mol	25.71
Heat of solution in water at 0 °C, kJ/mol	- 8.20
At 25 °C c	- 6.82
Heat of combustion of liquid at constant pressure, kJ/mol c	11867.9
Heat of formation at 273 K, kJ/mol c	-165.48
Free energy of formation at 273 K, kJ/mol c	-136.40
Critical temperature, °C	181.5
Critical pressure, MPa (atm)	6.40(63.2)
Dipole moment, C-m (debyes)	9.04 x 10 ^{- 30} (2.69)
Ionization potential, Ev	10.50
Dissociation constant at 0 °C, K a	0.7 x 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

2.2 CHEMICAL PROPERTIES:

Acetaldehyde is a highly reactive compound exhibiting the general reactions of aldehydes; under suitable conditions, the oxygen or any hydrogen can be replaced. Acetaldehyde undergoes numerous condensation, addition, and polymerization reactions.

2.2.1 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). There have been many investigations of the photolytic and radical – induced decomposition of acetaldehyde and deuterated acetaldehydes.

2.2.2 The Hydrate and Enol Form: In aqueous solutions, acetaldehyde exists in equilibrium with the hydrate, $\text{CH}_3\text{CH}(\text{OH})_2$. The degree of hydration can be computed from an equation derived by Bell and Clunie. The mean heat of hydration is -21.34 kJ/mol (89.29 kcal/mol); hydration has been attributed to hyper conjugation. The enol form, vinyl alcohol ($\text{CH}_2 = \text{CHOH}$) exists in equilibrium with acetaldehyde to the extent of approximately one molecule per 30,000. Acetaldehyde enol has been acetylated with ketene to form vinyl acetate.

2.2.3 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 isolated depends on reaction conditions. Acetic acid is produced commercially by the liquid – phase oxidation of acetaldehyde at 65°C with cobalt or manganese acetate dissolved in acetic acid as a catalyst. Liquid – phase oxidation of acetaldehyde in the presence of mixed acetates of copper and cobalt yields acetic anhydride. Peroxyacetic acid or a perester is believed to be the precursor of acetic acid and acetic anhydride. There are two commercial processes for the production of peracetic acid. Low temperature oxidation of acetaldehyde in the presence of metal salts, ultraviolet irradiation, or ozone yields acetaldehyde monoperoacetate, which can be decomposed to peracetic acid and acetaldehyde. Peracetic acid can also be formed directly by liquid – phase oxidation at $5 - 50^\circ\text{C}$ with a cobalt salt catalyst. The nitric acid oxidation of acetaldehyde yields glyoxal. Oxidations of p – xylene to terephthalic acid and of ethanol to acetic acid are activated by acetaldehyde.

2.2.4 Reduction: Acetaldehyde is readily reduced to ethanol. Suitable catalysts for vapor-phase hydrogenation are supported nickel and copper oxide. Oldenberg and Rose have studied the kinetics of the hydrogenation of acetaldehyde over a commercial nickel catalyst.

2.2.5 Polymerization: Paraldehyde, 2,4,6-trimethyl – 1,3,5 – trioxane, a cyclic trimer of acetaldehyde is formed when a mineral acid, such as sulfuric, phosphoric, or hydrochloric acid, is added to acetaldehyde. Paraldehyde can also be formed continuously by feeding

acetaldehyde as a liquid at 15 - 20°C over an acid ion – exchange resin. Depolymerization of paraldehyde occurs in the presence of acid catalysts. 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).

Metaldehyde, 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. Metaldehyde melts in a sealed tube at 246.2°C and sublimes at 115 °C with partial depolymerization.

Travers and Letort first discovered Polyacetaldehyde, rubbery polymer with an acetal structure, in 1936. More recently, it has been shown that white, nontacky, and highly elastic polymer can be formed by cationic polymerization with BF₃ in liquid ethylene. At temperatures below - 75°C with anionic initiators, such as metal alkyls in a hydrocarbon solvent, a crystalline, isotactic polymer is obtained. This polymer also has an acetal structure [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).

2.2.6 Reactions with aldehydes and ketones: The base catalyzed condensation of acetaldehyde leads to the dimer, acetaldol, which can be hydrogenated to form 1,3 butandiol or dehydrated to form crotonaldehyde. Crotonaldehyde can also be made directly by the vapor-phase condensation of acetaldehyde over a catalyst. Crotonaldehyde was formerly an important intermediate in the production of butyraldehyde, butanol, and 2-ethylhexanol. However it has been replaced completely with butyraldehyde from the oxo process. A small amount of crotonaldehyde is still required for the production of crotonic acid.

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 takes part in the condensation reactions and hydrogen exchange. A hexyl alcohol, 2-ethyl-1 butanol, is produced, industrially by the condensation of acetaldehyde and butaraldehyde in dilute caustic solution followed by hydrogenation of the acrolein 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.

The base catalyzed reaction of acetaldehyde with excess formaldehyde is the commercial route to pentaerythritol. The aldol condensation of three moles of form aldehyde with one mole of acetaldehyde is followed by a crossed cannizzaro reaction between pentaerythrose, the intermediate product, and formaldehyde to give pentaerythritol. The process proceeds to completion without isolation of the intermediate. Pantaerythrose has been made by condensing acetaldehyde and formaldehyde at $45^{\circ}C$ using magnesium oxide as a catalyst. The vapor-phase reaction of acetaldehyde and formaldehyde at $45^{\circ}C$ over a catalyst composed of lanthanum oxide on silica gel gives acrolein.

Ethyl acetate is produced commercially by the Tischenko condensation of acetaldehyde with an aluminum ethoxide catalyst. The Tischenko reaction of acetaldehyde with isobutyraldehyde yields a mixture of ethyl acetate, isobutyl acetate, and isobutyl isobutyrate.

2.2.7 Reactions with Ammonia and Amines: Acetaldehyde readily adds ammonia to form acetaldehyde ammonia. Diethyl amine is obtained when acetaldehyde is added to a saturated aqueous or alcoholic solution of ammonia and the mixture is heated to $50-75^{\circ}C$ in the presence of a nickel catalyst and hydrogen at $1.2 MP_a$ (12atm). Pyridine and pyridine derivates are made from paraldehyde and aqueous ammonia in the presence of a catalyst at elevated temperatures; acetaldehyde may also be used by the yields of pyridine are generally lower than when paraldehyde is the starting material. Levy and Othmer have studied the vapor- phase reaction of formaldehyde, acetaldehyde, and ammonia at $360^{\circ}C$ over oxide catalysts; a 49% yield of pyridine and picolines was obtained using an activated silica-alumina catalyst. Brown polymers result when acetaldehyde reacts with ammonia or amines at a PH of 6-7 and temperature of $3-25^{\circ}C$. With acetaldehyde, a

primary amines can be condensed to Schiff bases: $\text{CH}_3\text{CH}=\text{NR}$, the schiff base rivets to the starting materials in the presence of acids.

2.2.8 Reactions with Alcohols and Phenols: Alcohols add readily to acetaldehyde in the presence of a trace of mineral acid to form acetals; eg, ethanol and acetaldehyde form diethyl acetal. Similarly, cyclic acetals are formed by the reactions with glycols and other polyhydroxy compounds; eg, the reaction of ethylene glycol and acetaldehyde gives 2 – methyl – 1,3 – dioxolane.

Mercaptals, $\text{CH}_3\text{CH}(\text{SR})_2$, are formed in a like manner by the addition of mercaptans. The formation of acetals by a noncatalytic vapor – phase reactions of acetaldehyde and various alcohols at 350°C has been reported. Butadiene can be made by the reaction of acetaldehyde and ethyl alcohol at temperatures above 300°C over a tantala – silica catalyst. Aldol and crotonaldehyde are believed to be intermediates. Butyl acetate has been prepared by the catalytic reaction of acetaldehyde with butanol at 300°C .

Reaction of one mole of acetaldehyde with excess phenol in the presence of a mineral acid catalyst gives 1,1 – bis (p-hydroxyphenyl) ethane. With acid catalysts acetaldehyde and three moles or less of phenol yield soluble resins. Hardenable resins are difficult to produce by the alkaline condensation of acetaldehyde and phenol as acetaldehyde tends to undergo aldol condensation and self-resinification.

2.2.9 Reactions with Halogens and Halogen compounds: Halogens readily replace the hydrogen atoms of the methyl group: eg, chlorine reacts with acetaldehyde or paraldehyde at room temperature to give chloroacetaldehyde; increasing the temperature to $70^\circ\text{--}80^\circ\text{C}$ gives dichloroacetaldehyde; and at a temperature of $80\text{--}90^\circ\text{C}$ chloral is formed. The catalytic chlorination with an antimony powder or aluminum chloride ferric chloride has been described. Bromal is formed by an analogous series of reactions. It has been postulated that acetyl bromide is an intermediate in the bromination of acetaldehyde in aqueous ethanol. The gas – phase reaction of acetaldehyde and chlorine, has prepared acetyl chloride.

The oxygen atom in acetaldehyde can be replaced by reaction of the aldehyde with phosphorus pentachloride to produce 1,1 – dichloroethane. Hypochlorite and hypiodite react with acetaldehyde yielding chloroform and iodoform, respectively. Phosgene is produced by the reaction of carbon tetrachloride with acetaldehyde in the presence of anhydrous aluminum chloride. Chloroform reacts with acetaldehyde in the presence of potassium hydroxide and sodium amide to form 1,1,1 – trichloro – 2-propanol.

2.2.10 Miscellaneous Reactions: Sodium bisulfite adds to acetaldehyde to form a white crystalline addition compound, insoluble in ethyl alcohol and ether. The bisulfite addition compound frequently is used to isolate acetaldehyde from solution and for purification; the aldehyde is regenerated with dilute acid. Hydrocyanic acid adds to acetaldehyde in the presence of an alkali catalyst to form the cyanohydrin; the cyanohydrin may also be prepared by reaction of sodium cyanide with the bisulfite addition compound. Acrylonitrile can be made by reaction of acetaldehyde with hydrocyanic acid and heating the cyanohydrin to 600 – 700⁰C. Alanine can be prepared by reaction of ammonium salt and alkali metal cyanide with acetaldehyde; this is the Strecker amino acid synthesis, a general method for the preparation of α -amino acids. Grignard reagents add readily to acetaldehyde, the final product being a secondary alcohol. Thioacetaldehyde is formed by reaction of acetaldehyde with hydrogen sulfide; thioacetaldehyde polymerizes readily to the trimer.

Acetic anhydride adds to acetaldehyde forming ethylidene diacetate in the presence of dilute acid; boron fluoride is also a catalyst for the reaction. Ethylidene diacetate is decomposed to the anhydride and aldehyde at temperatures of 220-268⁰C and initial pressures of 1.5 – 6.1 kPa (110- 160 mm Hg), or by heating to 150⁰C with a zinc chloride catalyst. Acetone has been prepared in 90% yield by heating an aqueous solution of acetaldehyde to 410⁰C in the presence of a catalyst. Acetaldehyde can be condensed with active methylene groups. The reaction of isobutylene with aqueous solutions of acetaldehyde in the presence of 1-2% sulfuric acid yields alkyl-m-dioxanes, the principal product being 2,4,4,6-tetramethyl – m dioxane in yields up to 90%.

2.3 Uses:

The manufacturers use about 95% of the acetaldehyde produced internally as an intermediate for the production of other organic chemicals. Figure 1 illustrates the significant variety of organic products (and their end uses) derived from acetaldehyde.

Acetic acid and acetic anhydride are the derivatives of acetaldehyde followed by n-butanol and 2-ethylhexanol. Twenty percent of the acetaldehyde is consumed in variety of other products, the most important being pentaerythritol, trimethylolpropane, pyridines, peraceticacid, crotonaldehyde, chloral, lactic acid.