ALDEHYDES

1. Introduction

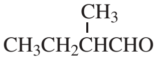
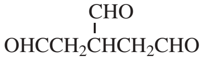
Aldehydes are carbonyl-containing organic compounds of the general formula $RCH{=}O$. The R group represents an aliphatic, aromatic, or heterosubstituted radical, except in formaldehyde, where R represents hydrogen. Aldehydes are inherently reactive compounds. The carbonyl group is susceptible to both oxidation and reduction, yielding acids and alcohols, respectively. Additionally, the carbonyl group is susceptible to nucleophilic addition, providing a means by which to form new chemical bonds. Furthermore, the presence of the carbonyl activates the hydrogens bound to the alpha carbon, and thus provides an additional site of reactivity. Ketones are a related class of compounds having two alkyl groups attached to the carbonyl group $R_1R_2C{=}O$ (see KETONES).

2. Nomenclature

The common method of naming aldehydes corresponds very closely to that of the related acids (see CARBOXYLIC ACIDS), in the sense that the term *aldehyde* is added to the base name of the acid. For example, formaldehyde (qv) comes from formic acid, acetaldehyde (qv) from acetic acid, and butyraldehyde (qv) from butyric acid. If the compound contains more than two aldehyde groups, or is cyclic, the name is formed using *carbaldehyde* to indicate the functionality. The IUPAC system of aliphatic aldehyde nomenclature is derived by replacing the final *-e* from the name of the parent acyclic hydrocarbon by the suffix *-al*. If two aldehyde functional groups are present, the suffix *-dial* is used. The prefix *formyl* is used with polyfunctional compounds. Examples of nomenclature types are shown in Table 1.

Kirk-Othmer Encyclopedia of Chemical Technology.

Table 1. **Aldehyde Nomenclature**

Structural formula	Name	CAS Registry Number
$H{-}CHO$	formaldehyde or methanal	[50-00-0]
CH_3CHO	acetaldehyde or ethanal	[75-07-0]
$(CH_3)_2CHCHO$	isobutyraldehyde or 2-methylpropanal or α-methylpropionaldehyde	[78-84-2]
$CH_3CH{=}CHCHO$	crotonaldehyde or 2-butenal	[4170-30-3]
 $CH_3CH_2\overset{CH_3}{\overset{\vert}{C}}HCHO$	2-methylbutyraldehyde or 2-methylbutanal	[96-17-3]
$OHCCH_2CH_2CH_2CHO$	glutaraldehyde or pentandial	[111-30-8]
 $OHCCH_2\overset{CHO}{\overset{\vert}{C}}HCH_2CHO$	1,2,3,-propanetricarbaldehyde or formylpentandial	[61703-13-7]
$OHCCH_2CH_2CH_2COOH$	4-formylbutanoic acid	[5746-02-1]
 $\underbrace{CH_2CH_2CH_2CH_2CH}CHO$	formylcyclopentane or cyclopentane-carbaldehyde	[872-53-7]

3. Physical Properties

The C_1 and C_2 carbon aliphatic aldehydes, formaldehyde and acetaldehyde are gases at ambient conditions whereas the C_3 (propanal [123-38-6]) through C_{11} (undecanal [112-44-7]) aldehydes are liquids, and higher aldehydes are solids at room temperature. As can be seen from Table 2, the presence of hydrocarbon branching tends to lower the boiling or melting point, as does unsaturation in the carbon skeleton. Generally, an aldehyde has a boiling point between those of the corresponding alkane and alcohol. Aldehydes are usually soluble in common organic solvents and, except for the C_1 to C_5 aldehydes, are only sparingly soluble in water. The lower, C_1 to C_8, aldehydes have pungent, penetrating, unpleasant odors, some of which may be attributed to the presence of the corresponding acids that readily form by air oxidation. Above C_8, aldehydes have more pleasant odors in their diluted state, and some higher aldehydes are used in the perfume and flavoring industries (see PERFUMES). Interestingly, the C_9 aldehyde, nonanal [124-19-6], is reported to possibly be a human sex pheromone (1). Aldehydes must be kept from contact with air (oxygen) to retain purity.

3.1. Spectroscopic Properties. Characteristic spectroscopic data for aldehydes are summarized in Table 3. The infrared (ir) carbonyl stretching frequency between 1720 and 1740 cm^{-1} in saturated aldehydes, is lowered when there is unsaturation in conjugation with the carbon–oxygen double bond. The carbonyl group also exhibits a weak ultraviolet (uv) absorption near 280 nm as a result of the excitation of one of the unshared electrons on the carbonyl oxygen n, to π^* transition).The nuclear magnetic resonance (nmr) absorptions

Table 2. **Properties of Aldehydes**

Name	CAS Registry Number	Formula	Molecular weight	Melting point, °C	Boiling point, °C	Refractive index at 25°C	Density 25°C, g/mL	Viscosity 25°C, cP	Surface tension at 25°C dyn/cm	Heat capacity at 25°C, J/g°K	Heat of vaporization NBP, kJ/mol	Solubility, at 25°C, g/100g water
Aliphatic aldehydes												
formaldehyde	[50-00-0]	HCHO	30.03	−92	−19.1		0.7328	0.1421	27.3797	2.3425	23.065	miscible
acetaldehyde	[75-07-0]	CH_3CHO	44.05	−123	20.85	1.3283	0.7744	0.2122	20.7644	2.5576	25.731	miscible
propionaldehyde	[123-38-6]	CH_3CH_2CHO	58.08	−103.15	48	1.3593	0.7912	0.3174	21.9551	2.3039	23.497	28.21
butanal (*n*-butyraldehyde)	[123-72-8]	$CH_3(CH_2)_2CHO$	72.11	−96.4	74.8	1.3766	0.7974	0.4192	24.9484	2.2705	31.056	7.64
2-methylpropanal (isobutyraldehyde)	[78-84-2]	$CH_3CH(CH_3)CHO$	72.11	−65	64.1	1.3698	0.7835	0.5211	20.3115	2.1608	31.234	6.38
pentanal (*n*-valeraldehyde)	[110-62-3]	$CH_3(CH_2)_3CHO$	86.13	−91.15	102.9	1.3917	0.8047	0.5054	25.326	2.1932	34.165	1.37
2-methyl butanal	[96-17-3]	$CH_3CH_2CH(CH_3)CHO$	86.13	<−100	91.3	1.3885	0.8007	0.525			32.35	<1.5
3-methylbutanal (isovaleraldehyde)	[590-86-3]	$CH_3CH(CH_3)CH_2CHO$	86.13	−105.5	92.9	1.3854	0.7915	0.51	22.6		32.397	<1.5
2,2-dimethylpropanal (pivalaldehyde)	[630-19-3]	$CH_3C(CH_3)_2CHO$	86.13	3.8	74.3	1.376	0.7749	0.64	21		30.198	1.43

hexanal (caproaldehyde)	[66-25-1]	$CH_3(CH_2)_4CHO$	100.16	−56	128.3	1.4017	0.8097	0.6625	25.9961	2.1560	36.558	0.60
heptanal (heptaldehyde)	[111-71-7]	$CH_3(CH_2)_5CHO$	114.19	−43.35	152.8	1.4094	0.8140	0.8619	26.5381	2.1793	38.827	<0.5
octanal (caprylaldehyde)	[124-13-0]	$CH_3(CH_2)_6CHO$	128.21	−27.15	174	1.4156	0.8181	1.1497	27.5748	2.0971	41.549	<0.5
2-ethylhexanal	[123-05-7]	$CH_3(CH_2)_3CH(C_2H_5)CHO$	128.21		164	1.4137	0.8152	1.0527	27.8571	1.9391	38.73	<0.5
nonanal (pelargonaldehyde)	[124-19-6]	$CH_3(CH_2)_7CHO$	142.24	−18	195	1.4208	0.8228	1.3563	28.3954	2.0755	43.67	<0.5
decanal (capraldehyde)	[112-31-2]	$CH_3(CH_2)_8CHO$	156.27	−6	215	1.4251	0.8213	1.5417	28.2958	2.0821	46.468	<0.5
Aromatic Aldehydes												
benzaldehyde	[100-52-7]	C_6H_5CHO	106.12	−57.13	178.7	1.5428	1.0415	1.3761	38.6152	1.6222	41.468	<0.5
phenylacetaldehyde	[122-78-1]	$(C_6H_5)CH_2CHO$	120.15		195		1.0229			1.8240	44.357	<0.5
o-tolualdehyde	[529-20-4]	$CH_3(C_6H_4)CHO$	120.15	−38.15	201	1.546	1.0315	2.2214	40.2099	1.6878	43.522	<0.5
m-tolualdehyde	[620-23-5]	$CH_3(C_6H_4)CHO$	120.15	−22.15	199	1.5389	1.0153	1.6629	37.6454	1.7493	44.782	<0.5
p-tolualdehyde	[104-87-0]	$CH_3(C_6H_4)CHO$	120.15		204		1.0093	1.8282	36.285	1.5101	45.61	<0.5
salicylaldehyde (*o*-hydroxybenzaldehyde)	[90-02-8]	$HO(C_6H_4)CHO$	122.12	1.6	196.5	1.57017	1.1491	2.4911	42.1437	1.8264	45.565	1.7
p-anisaldehyde (*p*-methoxybenzaldehyde)	[123-11-5]	$CH_3O(C_6H_4)CHO$	136.15	0	249.1	1.5707	1.1965				51.182	0.2

Table 3. **Spectroscopic Absorptions of Aldehydes**

Compound	ir, cm^{-1}[a]	uv, nm	^{1}H nmr, ppm[b]	^{13}C nmr, ppc[c]
acetaldehyde	1730	290	9.80	200
butyraldehyde	1725	283	9.74	202
benzaldehyde	1695	278	10.00	192
2-butenal	1700	301	9.48	193

[a] Carbonyl stretching frequency.
[b] Aldehyde proton, relative to TMS.
[c] Carbonyl carbon, relative to TMS.

of carbonyl proton (^{1}H-nmr) and carbon (^{13}C-nmr) are very characteristic and highly informative. The proton attached to the carbonyl exhibits a strong downfield resonance (~10 ppm) relative to the standard tetramethylsilane (TMS), as does the carbonyl carbon that appears at ~200 ppm, again relative to TMS. The downfield shift of the nmr resonances and the intensity of the ir stretching frequency are attributable to the polar nature of the carbon–oxygen double bond.

4. Chemical Properties

Aldehydes are very reactive compounds. Reactions generally fall into two classes: those directly involving the carbonyl group and those occurring at the adjacent carbon atom. The polar nature of the carbonyl group($\mathrm{RC\overset{\delta+}{H} = \overset{\delta-}{O}}$) lends itself to nucleophilic addition, reduction and oxidation, and also affects the reactivity of its adjacent carbon atom by rendering its hydrogens relatively acidic. Aldehydes having acidic hydrogens (also known as active methylene compounds) must be protected against inadvertent contact with bases, as such contact may result in an exothermic condensation reaction that may become dangerous. There are many available references offering detailed descriptions of aldehyde reactions (2–6). Many of the reactions involving aldehydes have been named for their discoverers and comprehensive reviews of name reactions are also available (7–9).

4.1. Reduction Reactions. Aldehydes can be reduced to the corresponding alcohols by catalytic hydrogenation using heterogeneous, as well as homogeneous catalysts.

$$CH_3CH_2CH_2CHO \xrightarrow[\text{catalyst}]{H_2} CH_3CH_2CH_2CH_2OH$$

Common heterogeneous catalyst compositions contain oxides or salts of platinum, nickel, copper, cobalt, or palladium and are often present as mixtures of more than one metal. Homogeneous catalysts consist of trialkylphosphine complexes of transition metals such as rhodium, cobalt, and ruthenium. Metal hydrides, such as lithium aluminum hydride [16853-85-3] or sodium borohydride [16940-66-2], can also be used to reduce aldehydes. Depending on additional functionalities that may be present in the aldehyde molecule, specialized reducing reagents such as trimethoxyaluminum hydride or alkylboranes (less reactive and more selective) may be used. Other less industrially significant reduction procedures such as the Clemmensen reduction or the modified Wolff–Kishner reduction exist as well.

4.2. Oxidation Reactions. In general, aldehyde are easily oxidized in air to the corresponding carboxylic acid, by a free-radical chain reaction.

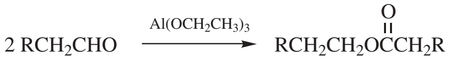
$$\mathrm{RCHO} \xrightarrow[\text{catalyst}]{O_2} \mathrm{RCOOH}$$

Air or oxygen are commonly used, with or without the homogeneous metal catalysts. This is the basis for many industrially significant preparations, eg, acetaldehyde to acetic acid [64-19-7] (see ACETIC ACID AND DERIVATIVES), propionaldehyde to propionic acid [79-09-47], furfural [98-01-1] to furoic acid [26447-28-9], and acrolein toacrylic acid [79-10-7] (see ACRYLIC ACID AND DERIVATIVES). For specialty applications, a variety of oxidizing reagents are available to perform this transformation. Although both chromium and manganese compounds can be used, an aqueous solution of potassium permanganate [7722-64-7] under either acidic or basic conditions is the more commonly employed reagent. Other known reagents for the oxidation of aldehydes include, hydrogen peroxide, nitric acid and a suspension of silver oxide in aqueous alkali. The latter provides a very mild and selective method for this type of oxidation.

Aldehydes can undergo an intermolecular oxidation–reduction (Cannizzaro reaction) by the action of strong base to produce a carboxylic acid salt and an alcohol. This reaction is common to aromatic aldehydes, and aliphatic ones with no α-hydrogen atoms.

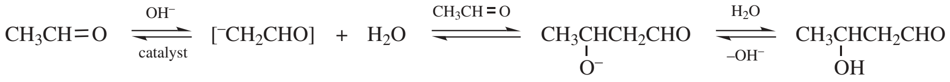
$$2\ C_6H_5CHO \xrightarrow{\mathrm{NaOH}} C_6H_5CH_2OH + C_6H_5CO_2Na$$

A related oxidation–reduction of aldehydes with α-hydrogens is the Tischenko reaction. This reaction occurs by the action of aluminum ethoxide, and the product is an ester.



$$2\ \mathrm{RCH_2CHO} \xrightarrow{\mathrm{Al(OCH_2CH_3)_3}} \mathrm{RCH_2CH_2O}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{CH_2R}$$

4.3. Addition Reactions. *Aldol Addition.* The hydrogen atoms on the carbon adjacent to the aldehyde carbonyl are relatively acidic and can be abstracted by strong bases. The resulting carbon anion,



$$\mathrm{CH_3CH{=}O} \underset{\text{catalyst}}{\overset{OH^-}{\rightleftharpoons}} [^-\mathrm{CH_2CHO}] + H_2O \overset{\mathrm{CH_3CH{=}O}}{\rightleftharpoons} \mathrm{CH_3}\underset{\underset{\displaystyle O^-}{|}}{\mathrm{C}}\mathrm{HCH_2CHO} \underset{-OH^-}{\overset{H_2O}{\rightleftharpoons}} \mathrm{CH_3}\underset{\underset{\displaystyle OH}{|}}{\mathrm{C}}\mathrm{HCH_2CHO}$$

also known as enolate, adds to the carbonyl of another aldehyde molecule to form a dimer adduct which is protonated to the alcohol-aldehyde product known as aldol.

Aldehyde dimerization can also occur with acid catalysts. The name aldol was introduced by Wurtz in 1872 to describe the product resulting from the acid-catalyzed reaction of acetaldehyde. The aldol products are not usually isolated; and they readily dehydrate to form α,β-unsaturated aldehydes. This overall transformation is commercially employed to produce 2-ethyl-2-hexenal [26266-68-2] often referred to as ethylpropylacrolein, from butyraldehyde (qv). The ethylpropylacrolein is then hydrogenated to produce 2-ethylhexanol, a commercially significant plasticizer alcohol (see ALCOHOLS, HIGHER ALIPHATIC). The next higher homologue, a C_{10} alcohol mixture containing 2-propylheptanol, can be produced in an analogous fashion from a valeraldehyde product mixture resulting from hydroformylating a mixed butenes stream (see BUTYLENES). This hydroformylation is accomplished using a new generation of highly active phosphite-promoted rhodium catalysts.

Claisen and Perkin Reactions. These reactions are similar to the aldol addition. The Claisen reaction is different than the better-known Claisen condensation of esters, and is carried out by combining an aromatic aldehyde and an ester in the presence of a strong base, such as sodium hydride, sodium amide, to give a β-hydroxy ester that dehydrates to an α,β-unsaturated ester.

$$C_6H_5CHO + CH_3CO_2C_2H_5 \xrightarrow[0-5^\circ C]{NaH} C_6H_5CH{=\!=}CHCO_2C_2H_5$$

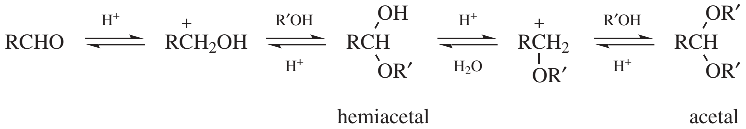
The Perkin reaction, utilizing an aromatic aldehyde, an acid anhydride, and a base such as an acid salt or amine, produces the corresponding α,β-unsaturated acid.

$$C_6H_5CHO \;+\; (CH_3CO_2)O \xrightarrow{(CH_3CH_2)_3N} C_6H_5CH{=}CHCOOH \;+\; CH_3COOH$$

Analogously, aldehydes react with ammonia [7664-41-7] or primary amines to form Schiff bases. Subsequent reduction produces amine. Other synthetically useful reactions include the addition of hydrogen cyanide [74-90-8], sodium bisulfite [7631-90-5], amines, or thiols to the carbonyl group, and usually requires the use of a catalyst to assist in reaching the desired equilibrium product.

Addition of Alcohols. This acid catalyzed reaction leads to the formation of a class of compounds known as acetals. The first addition product, a hemiacetal, is unstable, the equilibrium generally favoring the parent aldehyde. Subsequent steps involve protonation of the —OH which leads to a stabilized carbonium ion, followed by reaction of a second alcohol molecule.

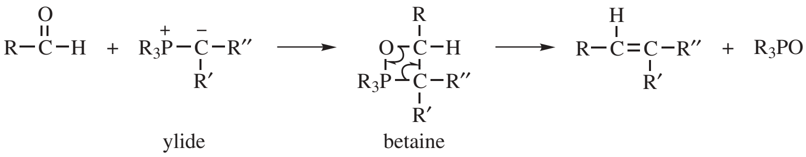
Acetals have been used in racing car fuels, gasoline additives, and paint and varnish solvents and



$$RCHO \xrightleftharpoons{H^+} \overset{+}{R}CH_2OH \xrightleftharpoons[H^+]{R'OH} RCH\begin{smallmatrix}OH\\OR'\end{smallmatrix} \xrightleftharpoons[H_2O]{H^+} \underset{OR'}{\overset{+}{R}CH_2} \xrightleftharpoons[H^+]{R'OH} RCH\begin{smallmatrix}OR'\\OR'\end{smallmatrix}$$

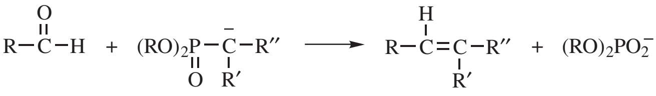
strippers. Acetals of higher aldehydes have fragrances similar to, but not so pungent as the parent aldehydes. Because they are not as sensitive to alkalies or autoxidation, acetals find use as fragrances for alkaline formulations such as soaps, shampoos and heavy-duty detergents.

The Wittig Reaction. In this very important reaction initially involving nucleophilic addition to an aldehyde carbonyl, an aldehyde reacts with a phosphorus **ylide** forming a **betaine** intermediate that decomposes to produce an olefin and a tertiary phosphine oxide.



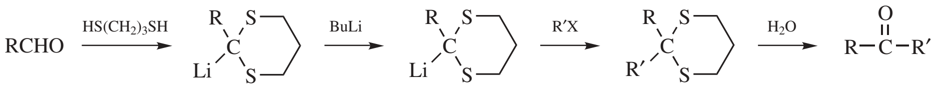
Perhaps the most notable example of this chemistry is in the production of vitamin A [68-26-8], where the β-ionylidenacetaldehyde is condensed with the ester-ylid to obtain the polyene ester. Reduction then yields vitamin A (see VITAMINS).

The Wittig reaction has been extended to include carbanions generated from phosphonates, which is often referred to as the Horner–Wittig or Horner–Emmons reaction.



The Horner–Emmons reaction has a number of advantages over the conventional Wittig reaction. It occurs with a wider variety of aldehydes and ketones under relatively mild conditions as a result of the higher nucleophilicity of the phosphonate carbanions. The separation of the olefinic product is easier due to the aqueous solubility of the phosphate by-product, and the phosphonates are readily available from the Arbusov reaction. Furthermore, although the reaction itself is not stereospecific, the majority favor the formation of the trans olefin and many produce the trans isomer as the sole product.

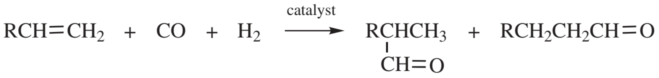
A useful synthetic application of aldehydes is as masked 1,3-dithianes. In these aldehyde derivatives, the normal mode of reaction of the carbonyl, which is to react with nucleophiles, is reversed (umpolung) and can react with electrophiles, if a proton in the 1,3-dithiane is first removed with butyllithium. The following sequence of reaction is a practical method for the converting an aldehyde into a ketone.



5. Manufacture

A complete discussion of synthetic procedures that yield aldehydes as products can be found in the literature (10, 11).

Of these methods only a few are used on industrial scale. One important industrial process for manufacture of aldehydes is by hydroformylation of olefins using synthesis gas and transition metal catalysts (oxo synthesis). This reaction was discovered in Germany in 1938 and commercialized in the 1950s for the production propionaldehyde from ethylene and butyraldehydes from propylene using cobalt catalyst (12).



$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} \underset{\displaystyle CH{=}O}{RCHCH_3} + RCH_2CH_2CH{=}O$$

Current commercial processes employ ligand-modified metal catalysts, which operate under milder conditions and provide better control of linear and branched aldehyde selectivities. Recent advances in hydroformylation technology include: catalysts promoted with phosphite ligands, which exhibit high reactivity with less reactive olefins under mild reaction conditions; novel catalyst–product separation technologies, which permit the manufacture of high molecular, weight aldehydes (C_7 to C_{15}) as well as more thermally sensitive aldehydes; fatty aldehydes, generally produced by dehydrogenation of corresponding alcohols in the presence of a suitable catalyst, can now be manufactured using oxo technology.

The direct oxidation of ethylene is used to produce acetaldehyde (qv) in the Wacker-Hoechst process. The catalyst system is an aqueous solution of palladium chloride and cupric chloride. Under appropriate conditions, an olefin can be oxidized to form an unsaturated aldehyde such as the production of acrolein [107-02-8] from propylene (see ACROLEIN AND DERIVATIVES).

Another commercial aldehyde synthesis is the catalytic dehydrogenation of primary alcohols at high temperature in the presence of a copper or a copper-chromite catalyst. Although there are several other synthetic processes employed, these tend to be smaller scale reactions. For example, acyl halides can be reduced to the aldehyde (Rosenmund reaction) using a palladium-on-barium sulfate catalyst. Formylation of aryl compounds, similar to hydroformylation, using HCN and HCl (Gatterman reaction) or carbon monoxide and HCl (Gatterman–Koch reaction) can be used to produce aromatic aldehydes.

$$ArH + CO \xrightarrow[\text{HCl}]{Cu_2Cl_2,\ AlCl_3} ArCHO$$

Additionally, Grignard reagent reacts with an alkyl orthoformate to form an acetal that is then hydrolyzed to the corresponding aldehyde using dilute acid.

$$CH_3CH_2MgX + HC(OR)_3 \xrightarrow[-Mg(OR)X]{} CH_3CH_2CH(OR)_2 \xrightarrow{\text{catalyst}} CH_3CH_2CHO + ROH$$

6. Production and Economic Aspects

From the list of commercially significant aldehydes in Table 4, formaldehyde is produced in the largest volume and has comparable economic value (volume × price) to that of butyraldehyde.

Table 4. **Annual Consumption of Aldehydes by Major Regions**[a]

Aldehyde	Thousands of metric tons per year U.S. and Canada	Europe	Asia and Japan	*World Total*	2000 prices, $/kg
formaldehyde	4630	7036	4504	*17553*	0.28
acetaldehyde	190	651	436		1.00
propionaldehyde	580	53			1.12
butyraldehyde	1566	1892	1901	*5701*	1.14
phenylacetaldehyde					37.9
salicylaldehyde					11
p-anisaldehyde					13.2

[a] *Chemical Economics Handbooks*-SRI international, 1999.

Table 5 contains a listing of representative aldehyde producers. Only the products identified in Table 4 have been included.

7. Characterization

Aldehydes can be characterized qualitatively through the use of Tollens' or Fehling's reagents as well as by spectroscopic means. The use of Tollens' reagent, a solution of silver nitrate in dilute, basic, aqueous ammonia, leads to the deposition of a silver mirror in the presence of an aldehyde. Fehling's reagent, an aqueous solution of copper sulfate, sodium potassium tartrate, and sodium hydroxide, produces a reddish brown precipitate of cuprous oxide in the presence of an aldehyde. Additionally, aldehyde carbonyl groups can be derivatized. Aldehyde oximes, phenylhydrazones, 2,4-dinitrohydrazones, semicarbazones, or sodium bisulfite addition products can be generated, purified, and characterized by their distinctive melting points. Hydrazone derivatives are often useful in isolating the aldehyde as a solid, crystalline material. The carbonyl group may also be oxidized to an acid through the use of hydrogen peroxide or potassium permanganate and the resultant carboxylic acid characterized by its spectroscopic properties and derivatives.

8. Health and Safety Factors

Interest in the toxicity of aldehydes has focused primarily on specific compounds, particularly formaldehyde, acetaldehyde, and acrolein (13). Little evidence exists to suggest that occupational levels of exposure to aldehydes would result in mutations, although some aldehydes are clearly mutagenic in some test systems. There are, however, acute effects of aldehydes.

8.1. Irritation and Sensitization. Low molecular weight aldehydes, the halogenated aliphatic aldehydes, and unsaturated aldehydes are particularly irritating to the eyes, skin, and respiratory tract. The mucous membranes

Table 5. **Aldehyde Producers**[a]

Company	Aldehyde product
	United States and Canada
Aristech Chemical Corp.	butyraldehyde
BASF Corp.	butyraldehyde
Borden Chemical	formaldehyde
Celanese Corporation	butyraldehyde, propionaldehyde, formaldehyde
Eastman	acetaldehyde, propionaldehyde, butyraldehyde
Firmenich Incorporated	phenylacetaldehyde
Georgia-Pacific Resins, Inc.	formaldehyde
Givauden-Roure Corporation	phenylacetaldehyde, *p*-anisaldehyde
Penta Manufacturing	*p*-anisaldehyde
Perstorp Polyols, Inc.	formaldehyde
Reichhold Limited	formaldehyde
Solutia Inc.	formaldehyde
Union Carbide	propionaldehyde, butyraldehyde
	Europe
BASF actiengesellschaft	formaldehyde, propionaldehyde, butyraldehyde, *p*-anisaldehyde, phenylacetaldehyde
Borden Chemical	formaldehyde
Celanese Chemicals Europe	acetaldehyde, butyraldehyde
Degussa- Hüls AG	formaldehyde
Givaudan-Roure SA	phenylacetaldehyde, *p*-anisaldehyde
Harmann & Reimer	phenylacetaldehyde, *p*-anisaldehyde
Hüls	acetaldehyde, butyraldehyde
Lonza	acetaldehyde
Neste Oxo AB	butyraldehyde
NORSOLOR	formaldehyde
Oxochimie SA	butyraldehyde
Perstorp Specialty Chemicals	formaldehyde
	East Asia
Chisso Corp.	butyraldehyde
Daicel Chemical Industries	phenylacetaldehyde
Eastman Chemical Singapore	butyraldehyde
Korea Alcohol Industries Co.	acetaldehyde
Kyowa Yuka Company	acetaldehyde, butyraldehyde
LG Chemical Ltd.	butyraldehyde
Lee Chang Yung Chem. Ind.	acetaldehyde, formaldehyde
Midori Kagaki Co.	*o*-anisaldehyde, *p*-anisaldehyde
Mitsubishi Chemical Corporation	formaldehyde, acetaldehyde, butyraldehyde
Mitsui	formaldehyde
Nippon Shokubai Co.	*p*-anisaldehyde
Petro Oxo Nusantara	butyraldehyde
Showa Denko K. K.	acetaldehyde, phenylacetaldehyde

[a] *Chemical Economics Handbooks*-SRI international, 1999.

of nasal and oral passages and the upper respiratory tract can be affected, producing a burning sensation, an increased ventilation rate, bronchial constriction, choking, and coughing. If exposures are low, the initial discomfort may abate after 5–10 min but will recur if exposure is resumed after an interruption. Furfural, the acetals, and aromatic aldehydes are much less irritating than formaldehyde and acrolein. Reports of sensitization reactions to formaldehyde are numerous.

8.2. Anesthesia. Materials that have unquestionable anesthetic properties arechloral hydrate [302-17-0], paraldehyde, dimethoxymethane [109-87-5], and acetaldehyde diethyl acetal. In industrial exposures, however, any action as an anesthesia is overshadowed by effects as a primary irritant, which prevent voluntary inhalation of any significant quantities. The small quantities that can be tolerated by inhalation are usually metabolized so rapidly that no anesthetic symptoms occur.

8.3. Organ Pathology. The principal pathology experimentally produced in animals exposed to aldehyde vapors is that of damage to the respiratory tract and pulmonary edema. In general, the aldehydes are remarkably free of actions that lead to definite cumulative organic damage to tissues. Thus the aldehydes cannot generally be regarded as potent carcinogens. Noted, however, that in chronic animal studies conducted by inhalation, formaldehyde has induced tumors of the nasal tissue. On the other hand, isobutyraldehyde has not produced a similar carcinogenic effect in similarly designed studies. Moreover, the intolerable irritant properties of the compounds preclude substantial worker exposure under normal conditions.

There is a significant difference in the toxicological effects of saturated and unsaturated aliphatic aldehydes. As can be seen in Table 6, the presence of the double bond considerably enhances toxicity. The precautions for handling reactive unsaturated aldehydes such as acrolein, methacrolein [78-85-3], and crotonaldehyde should be the same as those for handling other highly active eye and pulmonary irritants, as, eg, phosgene.

Material Safety Data Sheets, (MSDS), for individual compounds should be consulted for detailed information. Precautions for the higher aldehydes are essentially those for most other reactive organic compounds and should include: adequate ventilation in areas where high exposures are expected; fire and explosion precautions; and proper instruction of employees in use of respiratory, eye, and skin protection.

Table 6. **Effect of Unsaturation on Toxicity of Aldehydes**

Compound	Formula	LC_{50}, ppm[a]	LD_{50}, mg/kg[b]	TWA[c]
acetaldehyde	CH_3CHO	20,000	1,930	200
propionaldehyde	CH_3CH_2CHO	26,000	1,410	
acrolein	$CH_2{=}CHCHO$	130	25.9	0.1
isobutyraldehyde	$(CH_3)_2CHCHO$	>8,000[d]	2810	
methacrolein	$CH_2{=}C(CH_3)CHO$	250[d]	111	
n-butyraldehyde	$CH_3(CH_2)_2CHO$	60,000	2,490	
crotonaldehyde (2-butenal)	$CH_3CH{=}CHCHO$	1,400	260	2

[a] In rats, an exposure time of 30 min.

[b] In rats, dosage administered orally.

[c] Occupational Safety and Health Administration (OSHA PEL).

[d] Exposure time of 4 h.

9. Uses

Aldehydes find the most widespread use as chemical intermediates. The production of acetaldehyde, propionaldehyde, and butyraldehyde as precursors of the corresponding alcohols and acids are examples. The aldehydes of low molecular weight are also condensed in an aldol reaction to form derivatives that are important intermediates for the plasticizer industry (see PLASTICIZERS). As mentioned earlier, 2-ethylhexanol, produced from butyraldehyde, is used in the manufacture of di(2-ethylhexyl) phthalate [117-87-7]. Aldehydes are also used as intermediates for the manufacture of solvents (alcohols and ethers), resins, and dyes. Isobutyraldehyde is used as an intermediate for production of primary solvents and rubber antioxidants (see ANTIOXIDANTS). Fatty aldehydes C_8 to C_{13} are used in nearly all perfume types and aromas (see PERFUMES). Polymers and copolymers of aldehydes exist and are of commercial significance.

BIBLIOGRAPHY

"Aldehydes" in *ECT* 1st ed., Vol. 1, pp. 334–342 by E. F. Landau, Celanese Corporation of America, E. I. Becker, Polytechnic Institute of Brooklyn, and O. C. Dermer, Oklahoma Agricultural and Mechanical College; in *ECT* 2nd ed., Vol. 1, pp. 639–648 by L. J. Fleckenstein, Eastman Kodak Co.; in *ECT* 3rd ed., Vol. 1, pp. 790–798, by P. D. Sherman, Union Carbide Corporation; in *ECT* 4th ed., Vol. 1, pp. 926–937 by David J. Miller, Union Carbide Chemicals and Plastics Corporation; " Aldehydes" in *ECT* (online), Posting date: December 4, 2000 by David J. Miller, Union Carbide Chemicals and Plastics Corporation.

CITED PUBLICATIONS

1. J. Buckingham, *Dictionary of Organic Compounds*, 5th ed., Chapman and Hall, New York, 1982.
2. S. Patai, *The Chemistry of the Carbonyl Group*, Wiley-Interscience, New York, 1966 and 1970.
3. H. O. House, *Modern Synthetic Reactions*, 2nd ed., W. A. Benjamin, Inc., Menlo Park, Calif., 1972.
4. C. D. Gutche, *The Chemistry of Carbonyl Compounds*, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1967.
5. A. T. Nielson and W. J. Houlihan, *Organic Reactions*, Vol. 16, John Wiley & Sons, Inc., New York, 1968.
6. T. Mukaiyama, *Organic Reactions*, Vol. 28, John Wiley & Sons, Inc., New York, 1982.
7. A. R. Surrey, *Name Reactions in Organic Chemistry*, 2nd ed., Academic Press, Inc., New York, 1961.
8. R. C. Denny, *Named Organic Reactions*, Plenum Press, New York, 1969.
9. H. Krauch and W. Kunz, *Organic Name Reactions*, 2nd ed., translated by J. M. Harkin, John Wiley & Sons, Inc., New York, 1964.
10. G. Hilgetag and A. Martini, eds., *Preparative Organic Chemistry*, 4th ed., Wiley-Interscience, New York, 1972, pp. 301–400.
11. I. T. Harrison, ed., *Compendium of Organic Synthetic Methods*, Vol. 1, 1971, pp. 132–176; Vol. 2, I. T. Harrison, ed., 1974, pp. 53–69; Vol. 3, L. S. Hegedus and L. G. Wade, Jr., eds., 1977, pp. 66–87; Vol. 4, L. G. Wade, Jr., ed., 1980, pp. 73–101; Vol. 5,

L. G. Wade, Jr., ed., 1984, pp. 92–123; Vol. 6, M. B. Smith, ed., 1988, pp. 51–66, Wiley- Interscience, New York.

12. B. Cornils and W. A. Herrmann, eds., *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1. pp. 29–90. VCH Publishers, New York, 1996,
13. F. A. Patty, *Patty's Industrial Hygiene and Toxicology*, John Wiley & Sons, Inc., New York, 1981, pp. 2629–2669.

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