ACROLEIN AND DERIVATIVES

Acrolein (2-propenal) (C_3H_4O) [107-02-8], is the simplest unsaturated aldehyde (CH_2=CHCHO). The primary characteristic of acrolein is its high reactivity due to conjugation of the carbonyl group with a vinyl group. Controlling this reactivity to give the desired derivative is the key to its usefulness. Acrolein now finds commercial utility in several major products as well as a number of smaller volume products. More than 80% of the refined acrolein that is produced today goes into the synthesis of methionine. Much larger quantities of crude acrolein are produced as an intermediate in the production of acrylic acid. More than 85% of the acrylic acid produced worldwide is by the captive oxidation of acrolein. Several review articles (1–8) and a book (9) have been published on the preparation, reactions, and uses of acrolein.

Acrolein is a highly toxic material with extreme lacrimatory properties. At room temperature, acrolein is a liquid with volatility and flammability somewhat similar to acetone; but unlike acetone, its solubility in water is limited. Commercially, acrolein is always stored with hydroquinone and acetic acid as inhibitors. Special care in handling is required because of the flammability, reactivity, and toxicity of acrolein.

The physical and chemical properties of acrolein are given in Table 1. Additional data are available (9–12).

1. Manufacture

Acrolein was first reported in 1843 but was not produced commercially until the late 1930s. The first commercial processes were based on the vapor-phase condensation of acetaldehyde and formaldehyde (1). In the 1940s, a series of catalyst developments based on cuprous oxide and cupric selenites led to a vapor-phase propylene oxidation route to acrolein (13,14). In 1959, Shell was the first to commercialize the propylene oxidation route to acrolein. These early propylene oxidation catalysts were capable of only low per pass propylene conversions (~15%) and therefore required significant recycle of unreacted propylene (15–17). In

Table 1. **Properties of Acrolein**

Property	Value
Physical properties	
molecular formula	C_3H_4O
molecular weight	56.06
specific gravity at 20/20°C	0.8427
coefficient of expansion at 20°C, vol/°C	0.00140
boiling point, °C	
at 101.3 kPa[a]	52.69
at 1.33 kPa[a]	−36
vapor pressure at 20°C, kPa[a]	29.3
heat of vaporization at 101.3 kPa[a], kJ/kg[b]	510
critical temperature, °C	233
critical pressure, MPa[c]	5.07
critical volume, mL/mol	189
freezing point, °C	−87.0
solubility at 20°C, % by wt	
in water	20.6
water in	6.8
refractive index, n^{20}_D	1.4013
viscosity at 20°C, mPa·s (=cP)	0.35
heat capacity (specific), kJ/(kg·K)[b]	
liquid (25°C)	2.16
gas (25°C)	1.42
liquid density at 20°C, kg/L[d]	0.8412
Chemical properties	
flash point, open cup	−18°C
closed cup	−26°C
flammability limits in air, vol %	
upper	31
lower	2.8
autoignition temperature in air, °C	234
heat of combustion of 25°C, kJ/kg[b]	− 27,589
heat of polymerization (vinyl), kJ/mol[b]	− 71–80
heat of condensation (aldol), kJ/mol[b]	− 42

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert kJ to kcal, divide by 4.184.
[c] To convert MPa to psi, multiply by 145.
[d] To convert kg/L to lb/gal, multiply by 8.345.

1957, Standard Oil of Ohio (Sohio) discovered bismuth molybdate catalysts capable of producing high yields of acrolein at high propylene conversions (>90%) and at low pressures (18). Over the next several decades, much industrial and academic research and development was devoted to improving these catalysts, which are used in the production processes for acrolein, acrylic acid, and acrylonitrile. All commercial acrolein manufacturing processes known today are based on propylene oxidation and use bismuth molybdate-based catalysts.

Many key improvements and enhancements to the bismuth molybdate based propylene oxidation catalysts have occurred since its discovery in 1957. Table 2 shows a chronological list of representative bismuth molybdate catalysts from the patent literature.

Table 2. **Propylene Oxidation Catalyst for Acrolein Production**

Year	Catalyst	Company	Reference
1960	BiMo	Sohio	18
1965	BiMoFe	Knapsack	19
1969	BiMoFeNiCo	Nippon Kayaku	20,21
1970	BiMoFeNiCrSn	Toa Gosei	22
1972	BiMoFeNiPTlMg	Sumitomo	23
1974	BiMoFeCoWSiK	Nippon Shokubai	24,25
1990	BiMoFeCoNiPKSmSi	Degussa	26
1992	BiMoFeCoNiNaCaBKSi	Mitsubishi Pet. Co.	27
1997	BiMoFeCoWSiKZrS	Nippon Shokubai	28
1999	BiMoFeCoWSbZnK	Mitsubishi Rayon	29

The most efficient catalysts are complex mixed-metal oxides that consist largely of Bi, Mo, Fe, Ni, and/or Co, K, and either P, B, W, or Sb (30). Many additional combinations of metals have been patented, along with specific catalyst preparation methods to adjust specific surface area, pore volume, and pore size distribution. Most catalysts used commercially today are extruded neat metal oxides as opposed to supported (coated) catalysts. Propylene conversions are generally >93%. Acrolein selectivities of 80–90% are typical. The acrolein yields depend not only on the chemical composition of the catalyst, but also on the shape of the catalyst and catalyst loading configurations.

With the maturing of the propylene oxidation catalyst area, attention in the 1980s and 1990s was more focused on reaction process related improvements. Alternate feedstocks such as propane have also been investigated but has not yet lead to a commercial process (31).

The catalytic vapor-phase oxidation of propylene is generally carried out in a fixed-bed multitube reactor at near atmospheric pressures and elevated temperatures (~350°C); molten salt or other heat exchange media is used for temperature control. Air is commonly used as the oxygen source and steam is added to suppress the formation of flammable gas mixtures. Operation can be single pass or a recycle stream may be employed. As catalyst technology matured, interest focused on improving process efficiency and minimizing process wastes by defining process improvements that use recycle of process gas streams and/or use of new reaction diluents (32–36).

The reaction is very exothermic. The heat of reaction of propylene oxidation to acrolein is 340.8 kJ/mol (81.5 kcal/mol); the overall reactions generate ~418 kJ/mol (100 kcal/mol). The principal side reactions produce acrylic acid, acetaldehyde, acetic acid, carbon monoxide, and carbon dioxide. A variety of other aldehydes and acids are also formed in small amounts. Proprietary processes for acrolein manufacture have been described (37, 38).

The reactor effluent gases are cooled to condense and separate the acrolein from unreacted propylene, oxygen, and other low boiling components (predominantly nitrogen). This is commonly accomplished in two absorption steps where (1) aqueous acrylic acid is condensed from the reaction effluent and absorbed in a water-based stream, and (2) acrolein is condensed and absorbed in water to separate it from the propylene, nitrogen, oxygen, and carbon oxides. Acrylic acid may

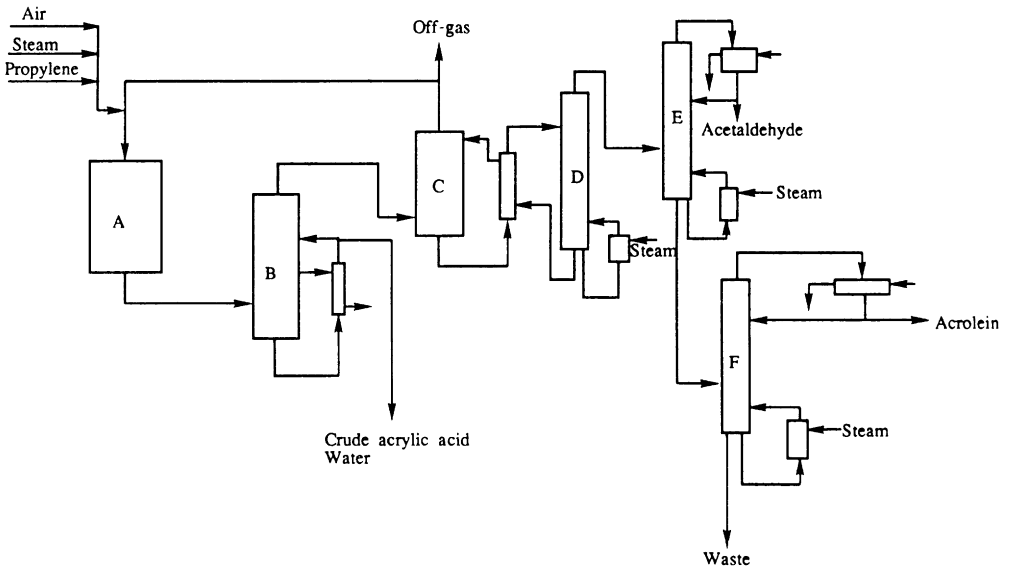


Fig. 1. A typical process flowsheet for acrolein manufacture. A, Fixed-bed or fluid-bed reactor; B, quench cooler; C, absorber; D, stripper; E and F, fractionation stills.

be recovered from the aqueous product stream if desired. Subsequent distillation separate water and acetaldehyde from the crude acrolein. In another distillation column, refined acrolein is recovered as an azeotrope with water. A typical process flow diagram is given in Figure 1.

2. Economic Aspects

Presently, the worldwide-refined acrolein nameplate capacity is ~250,000 t/yr. Both manufactures in the United States, Degussa and Dow have increased their production capacity in recent years to a total of ~122,000 t/yr. The key producers of refined acrolein are as noted in Table 3.

Of these producers, Elf Atochem, Degussa, and Daicel are reported to be in the merchant acrolein business. Dow supplies only to the acrolein derivative markets. Aventis also produces acrolein, primarily as a nonisolated intermediate to make methionine. A number of other small scale plants are located worldwide, which also produce acrolein as an intermediate to make methionine.

The significance of industrial acrolein production may be clearer if one considers the two major uses of acrolein—direct oxidation to acrylic acid and reaction to produce methionine via 3-methylmercaptopropionaldehyde (MMP). In acrylic acid production, acrolein is not isolated from the intermediate production stream. The 2000 acrylic acid production demand in the United States alone accounted for >1,300,000 t/yr (40), with worldwide capacity approaching 2,100,000 t/yr (41). Approximately 0.75 kg of acrolein is required to produce

Table 3. **Refined Acrolein Producers**

Producer	Annual nameplate capacity, 10^3 t/yr[a]
Degussa	110
Dow	72
Elf Atochem	30
Volzhskiy Orgsynthese	8
Daicel	9
Ohita	4.5
Sumitomo	15
(China)	4

[a]Estimated (39).

1 kg of acrylic acid. The methionine production process involves the reaction of acrolein with methyl mercaptan to produce the intermediate, MMP, which is further reacted with HCN to form methionine. Worldwide methionine capacity was estimated at ~570,000 t/yr in 2000 (42, 43) (see ACRYLIC ACID AND DERIVATIVES; AMINO ACIDS, SURVEY.)

3. Specifications and Analysis

Acrolein is produced according to the specifications in Table 4. Acetaldehyde and acetone are the principal carbonyl impurities in freshly distilled acrolein. Acrolein dimer accumulates at 0.50% in 30 days at 25°C. Analysis by two gas chromatographic (gc) methods with thermal conductivity detectors can determine all significant impurities in acrolein. The analysis with 0.91 mm × m 6.4 mm Porapak Q, 175–300 μm (50–80 mesh), programmed from 60 to 250°C at 10°C/min, does not separate acetone, propionaldehyde, and propylene oxide from acrolein. These separations are made with 3.66 mm × m 6.4 mm 20% Tergitol E-35 on 250–350 μm (45–60 mesh) Chromosorb W, kept at 40°C until acrolein elutes and then programmed rapidly to 190°C to elute the remaining components.

Alternatively, a bonded poly(ethylene glycol) capillary column held at 35°C for 5 min and programmed to 190°C at 8°C/min may be employed to determine all components but water. The Karl–Fischer method for water gives inaccurate results.

Table 4. **Specifications for Acrolein**

Requirement	Limit
acrolein, wt%, min	95.5
total carbonyl compounds other than acrolein, wt %, max	1.5
hydroquinone, wt %	0.10–0.25
water, wt %, max	3.0
specific gravity, 20°/20°C	0.842–0.846
pH of 10% solution in water at 25°C, max	6.0

Hydroquinone can be determined spectrophotometrically at 292 nm in methanol after a sample is evaporated to dryness to remove the interference of acrolein. An alternative method is high-performance liquid chromatography (hplc) on 10-μm LiChrosorb RP-2 at ambient temperature with 2.0 mL/min of 20% (v/v) 2,2,4-trimethylpentane, 79.20% chloroform, and 0.80% methanol with uv detection at 292 nm.

4. Reactions and Derivatives

Acrolein is a highly reactive compound because both the double bond and aldehydic moieties participate in a variety of reactions.

Acrolein is readily oxidized to acrylic acid, ($C_3H_4O_2$) [79-10-7], by passing a gaseous mixture of acrolein, air, and steam over a catalyst composed primarily of molybdenum and vanadium oxides (see ACRYLIC ACID AND DERIVATIVES). This process has been reviewed in a number of articles (44–47). Virtually all of the acrylic acid produced in the United States is made by the oxidation of propylene via the intermediacy of acrolein.

$$CH_2{=}CH{-}CHO \xrightarrow{\text{cat}} CH_2{=}CHCOOH$$

Direct formation of acrylic acid esters by oxidation of acrolein in the presence of lower alcohols has been studied (48). The intermediacy of acrylic acid is thereby avoided in the manufacture of these important acrylic acid derivatives.

$$CH_2{=}CH{-}CHO + O_2 + ROH \longrightarrow CH_2{=}CH{-}CO_2R$$

Because of a lack of discrimination between the double bond and carbonyl moieties, direct hydrogenation of acrolein leads to the production of mixtures containing propanol (C_3H_8O) [71-28-8], propionaldehyde (C_3H_6O) [123-38-6], and allyl alcohol, (C_3H_6O) [107-18-6]. However, proper selection of reaction conditions allows the carbonyl (49–62) and olefin (63–68) moieties to be selectively reduced to allyl alcohol (see ALLYL ALCOHOL AND DERIVATIVES) and propionaldehyde (see ALDEHYDES), respectively (69–89).

$$CH_2{=}CH{-}CHO \longrightarrow CH_2{=}CH{-}CH_2OH$$

$$CH_2{=}CH{-}CHO \longrightarrow CH_3CH_2CHO$$

The vapor-phase reduction of acrolein with isopropyl alcohol in the presence of a mixed-metal oxide catalyst yields allyl alcohol in a one-pass yield of 90.4%, with a selectivity (82) to the alcohol of 96.4%.

The addition of alcohols to acrolein may be catalyzed by acids or bases. By the judicious choice of reaction conditions the regioselectivity of the addition may be controlled and alkoxy-propionaldehydes (90), acrolein acetals,

or alkoxypropionaldehyde acetals may be produced in high yields (91).

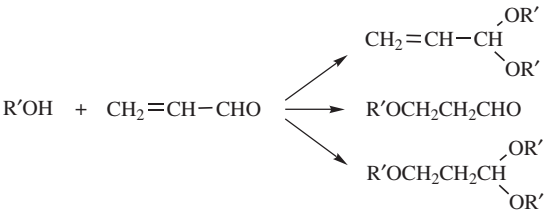
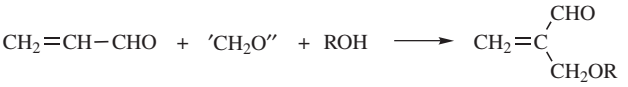


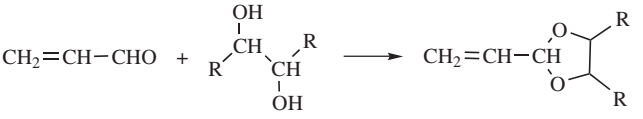
Table 5 lists a variety of alkoxypropionaldehydes and certain of their properties (92). Alcohols up to n-butyl have been added to acrolein in this fashion. Methyl, ethyl, and allyl alcohols react with ease, while the addition of hexyl or octyl alcohol proceeds in low yields. Although the alkoxypropionaldehydes have found only limited industrial utility, it is anticipated that they will find use as replacements for more toxic solvents. Furthermore, the alkoxypropionaldehydes may readily be reduced to the corresponding alkoxypropanols, which may also have desirable properties as solvents (93).

If the addition of alcohol to the olefin moiety of acrolein is carried out in the presence of a formaldehyde source, 2-(alkoxymethyl)acroleins are formed (94–97). 2-(Alkoxymethyl)acroleins are potential intermediates in the manufacture of substitued pyridines and quinolines.



Acrolein acetals have also been prepared in high yields (91). The formation of the acetal requires the careful control of reaction conditions to avoid additions to the double bond. Table 6 lists a variety of acrolein acetals that have been prepared and their boiling points (98).

The addition of certain glycols and polyols to acrolein leads to the production of cyclic acetal derivatives (99–103).



Cyclic acrolein acetals are, in general, easily formed, stable compounds and have been considered as components in a variety of polymer systems. Table 7 lists a variety of previously prepared cyclic acrolein acetals and their boiling points (104).

Reactions of acrolein with alcohols producing high yields of alkoxypropionaldehyde acetals are also known. Examples of these are displayed in Table 8 (105). The alkoxypropionaldehyde acetals may be useful as solvents or as intermediates in the synthesis of other useful compounds (106).

A new and potentially significant use of acrolein is the manufacture of 1,3-propanediol ($C_3H_6O_2$) [504-63-2] (107–109). Addition of water to acrolein forms

Table 5. **Alkoxypropionaldehydes from Acrolein**

Compound added	Product				
	Structure	CAS Registry Number	Molecular formula	bp, °C	Pressure at bp, kPa[a]
CH_3OH	$CH_3OCH_2CH_2CHO$	[2806-84-0]	$C_4H_8O_2$	49	6.7
C_2H_5OH	$C_2H_5OCH_2CH_2CHO$	[2806-85-1]	$C_5H_{10}O_2$	57	5.3
n-C_3H_7OH	*n*-$C_3H_7OCH_2CH_2CHO$	[19790-53-5]	$C_6H_{12}O_2$	88	12
iso-C_3H_7OH	iso-$C_3H_7OCH_2CH_2CHO$	[39563-51-4]	$C_6H_{12}O_2$	45	2
n-C_4H_9OH	*n*-$C_4H_9OCH_2CH_2CHO$	[13159-34-2]	$C_7H_{14}O_2$	60	2
$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2OCH_2CH_2CHO$	[44768-60-7]	$C_6H_{10}O_2$	55	1.9
$ClCH_2CH_2OH$	$ClCH_2CH_2OCH_2CH_2CHO$	[5422-33-3]	$C_5H_9ClO_2$	75.5	0.67
$CH_2{=}C(CH_3)CH_2OH$	$CH_2{=}C(CH_3)CH_2OHCH_2OCH_2CH_2CHO$	[76618-56-9]	$C_7H_{12}O_2$	62	1.2

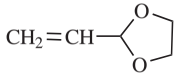
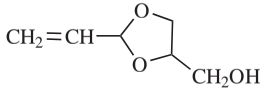
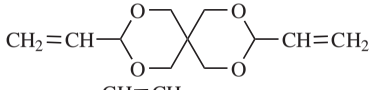
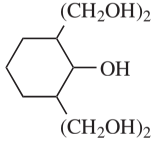
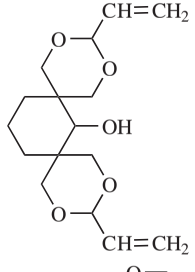
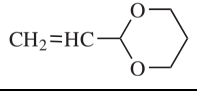
[a] To convert kPa to mm Hg, multiply by 7.5.

Table 6. **Acrolein Acetals**

Compound added	Product				
	Structure	CAS Registry Number	Molecular formula	bp, °C	Pressure at bp, kPa[a]
C_2H_5OH	$CH{=}CHCH(OC_2H_5)_2$	[3054-95-3]	$C_7H_{14}O_2$	63	12.1
CH_3OH	$CH_2{=}CHCH(OCH_3)_2$	[6044-68-4]	$C_5H_{10}O_2$	40	16
n-C_3H_7OH	$CH_2{=}CHCH(OC_3H_7)_2$	[20615-55-8]	$C_9H_{18}O_2$	87.5–88	
iso-C_3H_7OH	$CH_2{=}CHCH(Oiso\text{-}C_3H_7)_2$	[14091-80-6]	$C_9H_{18}O_2$	54	1.6
n-C_4H_9OH	$CH_2{=}CHCH(OC_4H_9)_2$	[45094-50-6]	$C_{11}H_{22}O_2$	39	1.6
$C_6H_5CH_2OH$	$CH_2{=}CHCH(OCH_2C_6H_5)_2$	[40575-57-3]	$C_{17}H_{18}O_2$	120	6.7×10^{-4}
$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH(OCH_2CH{=}CH_2)_2$	[3783-83-3]	$C_9H_{14}O_2$	75	3.7

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

Table 7. **Acrolein Cyclic Acetals**

Compound added	Structure	Product			
		CAS Registry Number	Molecular formula	bp, °C	Pressure at bp, kPa[a]
$HOCH_2CH_2OH$		[3984-22-3]	$C_5H_8O_2$	115.5–116.5	
$HOCH_2CH(OH)$-CH_2OH		[4313-32-0]	$C_6H_{10}O_3$	80	0.4
$C(CH_2OH)_4$		[78-19-3]	$C_{11}H_{16}O_4$	142–143 mp 41–42	1.6
		[b]	$C_{16}H_{24}O_5$	198–199	0.4
$HOCH_2CH_2CH_2OH$		[5935-25-1]	$C_6H_{10}O_2$	65–66	5.9

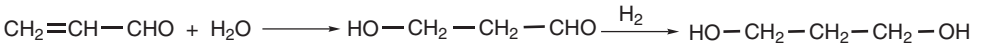
[a] To convert kPa to mm Hg, multiply by 7.5.
[b] No CAS Registry Number has been assigned.

Table 8. **Alkoxypropionaldehyde and Related Acetals**

Compound added	Product				
	Structure	CAS Registry Number	Molecular formula	bp, °C	Pressure at bp, kPa[a]
C_2H_5OH	$C_2H_5OCH_2CH_2CH(OC_2H_5)_2$	[7789-92-6]	$C_9H_{20}O_3$	69–70	1.3
CH_3OH	$CH_3OCH_2CH_2CH(OCH_3)_2$	[14315-97-0]	$C_6H_{14}O_3$	94–95	18.9
n-C_3H_7OH	$C_3H_7OCH_2CH_2CH(OC_3H_7)_2$	[53963-14-7]	$C_{12}H_{26}O_3$	109	1.6
i-C_3H_7OH	$C_3H_7OCH_2CH_2CH(O\text{iso-}C_3H_7)_2$	[89769-16-4]	$C_{12}H_{26}O_3$	89	1.5
$C_6H_5CH_2OH$	$C_6H_5CH_2OCH_2CH_2CH(OCH_2C_6H_5)_2$	[b]	$C_{24}H_{26}O_3$	243–246	0.07
$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2OCH_2CH_2$-$CH(OCH_2CH{=}CH_2)_2$	[8431-07-1]	$C_{12}H_{20}O_3$	113–114	1.3
n-C_4H_9OH	$C_4H_9OCH_2CH_2CH(OC_4H_9)_2$	[53963-15-8]	$C_{15}H_{32}O_3$	143–144	1.3
n-$C_5H_{11}OH$	$C_5H_{11}OCH_2CH_2CH(OC_5H_{11})_2$	[53963-17-6]	$C_{18}H_{38}O_3$	153–155	0.13
$ClCH_2CH_2OH$	$ClCH_2CH_2OCH_2CH_2CH(OCH_2CH_2Cl)_2$	[688-78-8]	$C_9H_{17}Cl_3O_3$	160–162	0.7
C_2H_5SH	$C_2H_5SCH_2CH_2CH(SC_2H_5)_2$	[19157-17-6]	$C_9H_{20}S_3$	143	1.3
C_2H_5SH + HCl	$ClCH_2CH_2CH(SC_2H_5)_2$	[19157-16-5]	$C_7H_{15}ClS_2$	115–117	1.5
$CH_2{=}CHCH_2OCH_2CH_2CHO$ + C_2H_5OH	$CH_2{=}CHCH_2OCH_2CH_2CH(OC_2H_5)_2$	[107023-55-2]	$C_{10}H_{20}O_3$	86	1.7
C_2H_5OH + HCl	$ClCH_2CH_2CH(OC_2H_5)_2$	[35573-93-4]	$C_7H_{15}ClO_2$	58–62	1.1
CH_3OH + HCl	$ClCH_2CH_2CH(OCH_3)_2$	[35502-06-8]	$C_5H_{11}ClO_2$	45	1.6
C_2H_5OH + HBr	$BrCH_2CH_2CH(OC_2H_5)_2$	[59067-07-1]	$C_7H_{15}BrO_2$	80–90	2.7
n-C_2H_7OH + HCl	$ClCH_2CH_2CH(OC_3H_7)_2$	[35502-07-9]	$C_9H_{19}ClO_2$	87	2.7
i-C_4H_9OH + HCl	$ClCH_2CH_2CH(O\text{i-}C_4H_9)_2$	[35502-09-1]	$C_{11}H_{23}ClO_2$	105	0.6

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] No CAS Registry Number has been assigned.

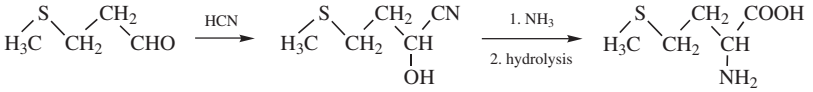
3-hydroxypropionaldehyde ($C_3H_6O_2$) [2134-29-4]. Hydrogenation of 3-hydroxypropionaldehyde forms 1,3-propanediol.



Competitive routes to 1,3-propanediol are ethylene oxide hydroformylation (110) and biofermentation of corn (111). The largest anticipated use of 1,3-propanediol is in the manufacture of polytrimethylene terephthalate (PTT). Shell and Dupont have announced commercial processes for this polyester.

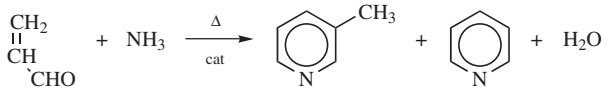
One of the largest uses of acrolein is the production of 3-methylmercaptopropionaldehyde, (C_4H_8OS) [3268-49-3], which is an intermediate in the synthesis of D,L-methionine ($C_5H_{11}NO_2S$) [59-51-8], an important chicken feed supplement.

3-Methylmercaptopropionaldehyde is also used to make the methionine hydroxy analogue $CH_3SCH_2CH_2CH(OH)COOH$, ($C_5H_{10}O_2S$) [583-91-5], which is used commercially as an effective source of methionine activity (112). All commercial syntheses of methionine and methionine hydroxy analogues are based on the use of acrolein as a raw material. More than 570,000 t of this amino acid are produced yearly (43) (see AMINO ACIDS). One method for the preparation of methionine from acrolein via 3-methylmercaptopropionaldehyde is as follows:



Methyl mercaptan adds to acrolein in nearly quantitative yields in the presence of a variety of basic catalysts (113–115). Other alkylmercaptopropionaldehydes produced by the reaction of acrolein with a mercaptan are known. Table 9 lists a variety of these and their boiling points (116).

Although the liquid-phase reaction of acrolein with ammonia produces polymers of little interest, the vapor-phase reaction, in the presence of a dehydration catalyst produces high yields of β-picoline, (C_6H_7N) [108-99-6] and pyridine, (C_5H_5N) [110-86-1] in a ratio of ~2:1.



β-Picoline may serve as an important source of nicotinic acid, ($C_6H_5NO_2$) [59-67-6] for dietary supplements. A variety of substituted pyridines may be prepared from acrolein (117–125).

Acrolein may participate in Diels–Alder reactions as the dieneophile or as the diene (126–130).

Table 9. **Alkylmercaptopropionaldehydes from Addition of Mercaptans to the Acrolein Double Bond**

	Product				
Compound added	Structure	CAS Registry Number	Molecular formula	bp, °C	Pressure at bp, kPa[a]
CH_3SH	$CH_3SCH_2CH_2CHO$	[3268-49-3]	C_4H_8OS	54–56	1.5
C_2H_5SH	$C_2H_5SCH_2CH_2CHO$	[5454-45-5]	$C_5H_{10}OS$	63–65	1.5
n-C_3H_7SH	n-$C_3H_7SCH_2CH_2CHO$	[44768-66-3]	$C_6H_{12}OS$	75	0.86
$C_6H_5CH_2SH$	$C_6H_5CH_2SCH_2CH_2CHO$	[16979-50-3]	$C_{10}H_{12}OS$	142.3	0.8
$CH_3C(O)SH$	$CH_3C(O)SCH_2CH_2CHO$	[53943-93-4]	$C_5H_8O_2S$	89	1.5
CF_3SH	$CF_3SCH_2CH_2CHO$	[58019-54-6]	$C_4F_3H_5OS$	46.5	2.7

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

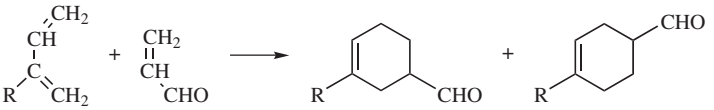
Table 10. **Products of Dienes Added to Acrolein**[a]

THBA Product[b]	CAS Registry Number	Time, h	bp, °C	Pressure at bp, kPa[c]
THBA	[100-50-5]	1	51–52	1.7
2,5-*endo*-methylene-THBA	[5453-80-5]	several[d]	70–72	2.7
4-methyl-THBA	[7560-64-7]	3	70–71	1.9
2,5-*endo*-ethylene-THBA	[40570-95-4]	8	84–85	1.6

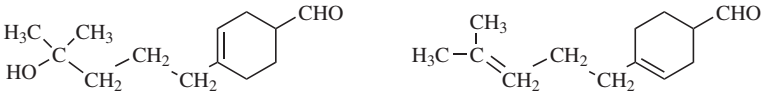
[a] Reaction at 100°C unless otherwise noted; yields are 90–95%.
[b] THBA from butadiene; 2,5-*endo*-methylene from 1,3-cyclopentadiene; 4-methyl-THBA from 2-methylbutadiene; 2,5-*endo*-ethylene from 1,3-cyclohexadiene.
[c] To convert kPa to mm Hg, multiply by 7.5.
[d] At 25°C.

The participation of acrolein as the dienophile in Diels–Alder reactions is, in general, an exothermic process. Dienes such as cyclopentadiene and 1-diethylamino-1,3-butadiene react rapidly with acrolein at room temperature.

Several Diels–Alder reactions in which acrolein participates as the dienophile are of industrial significance. These reactions involve butadiene or substituted butadienes and yield the corresponding 1,2,5,6-tetrahydrobenzaldehyde derivative (THBA); examples are given in Table 10 (131). These products have found use in the epoxy and perfume/fragrance industries.

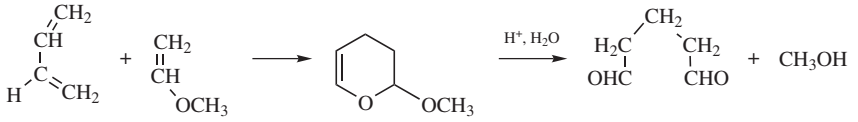


Many other acrolein derivatives produced via Diels–Alder reactions are classified as flavors and fragrances. Among those of commercial interest are lyral, ($C_{13}H_{22}O_2$), (1) [31906-04-4] (132, 133) and myrac aldehyde, ($C_{13}H_{20}O$), (2) [37677-14-8] (133, 134).



1 **2**

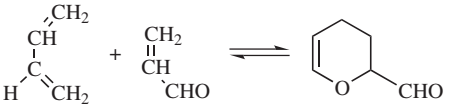
An industrially useful reaction in which acrolein participates as the diene is that with methyl vinyl ether. The product, methoxydihydropyran, ($C_6H_{10}O_2$) [4454-05-1] is an intermediate in the synthesis of glutaraldehyde, ($C_5H_8O_2$) [111-30-8].



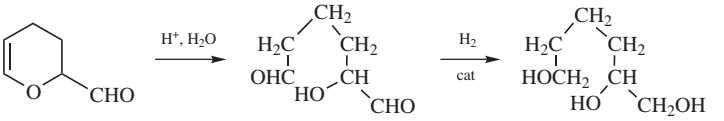
In addition to its principal use in biocide formulations (135), glutaraldehyde has been used in the film development and leather tanning industries (136). It

may be converted to 1,5-pentanediol, ($C_5H_{12}O_2$) [111-29-5] or glutaric acid ($C_5H_8O_4$) [110-94-1].

Acting as both the diene and dienophile, acrolein undergoes a Diels–Alder reaction with itself to produce acrolein dimer, 3,4-dihydro-2-formyl-2*H*-pyran, ($C_6H_8O_2$) [100-73-2]. At room temperature, the rate of dimerization is very slow. However, at elevated temperatures (~200°C) and pressures the dimer may be produced in single-pass yields of 33% with selectivities >95%. Acrolein is efficiently regenerated from its dimer by a retro-Diels–Alder reaction at temperatures near 500°C. Use of this reaction has been proposed for delivery of high purity acrolein at remote locations (137).



Acrolein dimer may be easily hydrated to α-hydroxyadipaldehyde, ($C_6H_{10}O_3$), [141-31-1] which may then be reduced to 1,2,6-hexanetriol, ($C_6H_{14}O_3$) [106-69-4]. Several uses for 1,2,6-hexanetriol, have been proposed including various polymer (in polyurethanes and polyesters), pharmaceutical, and cosmetics (as alternative to glycerol as a humectant) industry applications.



In the absence of inhibitors, acrolein polymerizes readily in the presence of anionic, cationic, or free-radical agents. The resulting polymers are insoluble, highly cross-linked solids with no known commercial use.

Copolymers, including one obtained by the oxidative copolymerization of acrolein with acrylic acid, a product of commercial interest, are known. There is a great variety of potential acrolein copolymers; however, significant commercial uses have not been developed. The possible application of polyacroleins or copolymers as polymeric reagents, polymeric complexing agents, and polymeric carriers has been recognized. Preparative methods as well as properties of the homopolymers and copolymers of acrolein have been reviewed (4, 9, 138).

5. Direct Uses of Acrolein

Because of its antimicrobial activity, acrolein has found use as an agent to control the growth of microbes in process feed lines, thereby controlling the rates of plugging and corrosion (see WASTES, INDUSTRIAL).

Acrolein at a concentration of <500 ppm is also used to protect liquid fuels against microorganisms. The dialkyl acetals of acrolein are also useful in this application. In addition, the growth of algae, aquatic weeds, and mollusks in recirculating process water systems is also controlled by acrolein. Currently, acrolein is used to control the growth of algae in oil fields and has also been

used as an H_2S scavenger (139). The ability to use acrolein safely in these direct applications is a prime concern and is a deterrent to more widespread use.

In recent years, several acrolein derivatives have been proposed to provide a safer means of transport of acrolein to an application site. Acrolein dimer is thermally cracked to acrolein at temperatures near 500°C (137). Acetals of acrolein, most particularly, vinyl dioxolane, may revert to acrolein and alcohol in acidified aqueous solution.

6. Health and Safety Factors

The most frequently encountered hazards of acrolein are acute toxicity from inhalation and ocular irritation (140). Because of its high volatility, even a small spill can lead to a dangerous situation. Acrolein is highly irritating and a potent lacrimator. The odor threshold (50%), 0.23 mg/m^3 [0.09 ppm (v/v)], is close to the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) and ACGIH TLV-TWA8, 0.25 mg/m^3 (0.1 ppm). The odor threshold for 100% recognition, 0.5 mg/m^3 (0.2 ppm), is above the TLV (141) but the OSHA and ACGIH short-term exposure limit (STEL) is 0.8 mg/m^3 (0.3 ppm), so perception of acrolein will generally provide adequate warning.

Concentrations of acrolein vapor as low as 0.6 mg/m^3 (0.25 ppm) may irritate the respiratory tract, causing coughing, nasal discharge, chest discomfort or pain, and difficulty with breathing (142). A concentration of 5–10 mg/m^3 (2–4 ppm) is intolerable to most individuals in a minute or two (140) and is close to the concentration considered immediately dangerous to life and health (143). At higher concentrations there may be lung injury from inhaled acrolein, and prolonged exposure may be fatal. In a short time, exposure to 25 mg/m^3 (10 ppm) or more is lethal to humans (144).

Acrolein vapor is highly irritating to the eyes, causing pain or discomfort in the eye, profuse lacrimation, involuntary blinking, and marked reddening of the conjunctiva. Splashes of liquid acrolein will produce a severe injury to the eyelids and conjunctiva and chemical burns of the cornea.

A small amount of acrolein may be fatal if swallowed. It produces burns of the mouth, throat, esophagus, and stomach. Signs and symptoms of poisoning may include severe pain in the mouth, throat, chest, and abdomen; nausea; vomiting, which may contain blood; diarrhea; weakness and dizziness; and collapse and coma (142).

Acrolein is highly toxic by skin absorption. Brief contact may result in the absorption of harmful and possibly fatal amounts of material. Skin contact causes severe local irritation and chemical burns. Butyl rubber gloves should be used when handling acrolein (145).

There is no specific antidote for acrolein exposure. Treatment of exposure should be directed at the control of symptoms and the clinical condition. Most of the harmful effects of acrolein result from its highly irritating and corrosive properties.

Chronic human exposure is unlikely due to the lack of tolerance to acrolein. There is no evidence that acrolein is a human carcinogen (146), and inadequate animal data preclude any evaluation of its carcinogenicity (147). Acrolein has

shown low, borderline, or moderate mutagenicity in bioassays, depending on the test system and frame of reference (148, 149). Animal studies that gave little indication of teratogenicity of acrolein are insufficient for determining whether acrolein is a teratogen (150). Some embryotoxicity over a narrow dose range with acrolein administered by injection indicates that acrolein is quite embryotoxic (150).

Acrolein is very flammable; its flash point is $<0^{\circ}C$, but a toxic vapor cloud will develop before a flammable one. The flammable limits in air are 2.8 and 31.0% lower and upper explosive limits, respectively, by volume. Acrolein is only partly soluble in water and will cause a floating fire, so alcohol type foam should be used in firefighting. The vapors are heavier than air and can travel along the ground and flash back from an ignition source.

Acrolein is a highly reactive chemical, and contamination of all types must be avoided. Violent polymerization may occur by contamination with either alkaline materials or strong mineral acids. Contamination by low molecular weight amines and pyridines such as α-picoline is especially hazardous because there is an induction period that may conceal the onset of an incident and allow a contaminant to accumulate unnoticed. After the onset of polymerization, the temperature can rise precipitously within minutes.

Acrolein reacts slowly in water to form 3-hydroxypropionaldehyde and then other condensation products from aldol and Michael reactions. Water dissolved in acrolein does not present a hazard. The reaction of acrolein with water is exothermic and the reaction proceeds slowly in dilute aqueous solution. This reaction will be hazardous in a two-phase adiabatic system in which acrolein is supplied from the upper layer to replenish that consumed in the lower, aqueous, layer. The rate at which these reactions occur will depend on the nature of the impurities in the water, the volume of the water layer, and the rate of heat removal. Thus a water layer must be avoided in stored acrolein.

Dimerization of acrolein is very slow at ambient temperatures but it can become a runaway reaction at elevated temperature ($\sim 90^{\circ}C$), a consideration in developing protection against fire exposure of stored acrolein.

7. Storage and Handling

The following cautions should be observed: Do not destroy or remove inhibitor. Do not contaminate with alkaline or strongly acidic materials. Do not store in the presence of a water layer. In the event of spillage or misuse that cause a release of product vapor to the atmosphere, thoroughly ventilate the area, especially near floor levels where vapors will collect.

Acrolein produced in the United States is stabilized against free-radical polymerization by 1000–2500 ppm of hydroquinone and is protected somewhat against base-catalyzed polymerization by ~100 ppm of acetic acid. To ensure stability, the pH of a 10% v/v solution of acrolein in water should be <6.

Since the principal hazard of contamination of acrolein is base-catalyzed polymerization, a "buffer" solution to shortstop such a polymerization is often employed for emergency addition to a reacting tank. A typical composition of this solution is 78% acetic acid, 15% water, and 7% hydroquinone. The acetic

acid is the primary active ingredient. Water is added to depress the freezing point and to increase the solubility of hydroquinone. Hydroquinone (HQ) prevents free-radical polymerization. Such polymerization is not expected to be a safety hazard, but there is no reason to exclude HQ from the formulation. Sodium acetate may be included as well to stop polymerization by very strong acids. There is, however, a temperature rise when it is added to acrolein due to catalysis of the acetic acid–acrolein addition reaction.

Suitable materials of construction are steel, stainless steel, and aluminum 3003. Galvanized steel should not be used. Plastic tanks and lines are not recommended.

Storage tanks should have temperature monitoring with alarms to detect the onset of reactions. The design should comply with all applicable industry, federal, and local codes for a class 1B flammable liquid. The storage temperature should be $<37.8^{\circ}C$. Storage should be under an atmosphere of dry nitrogen and should vent vapors from the tank to a scrubber or flare.

In treatment of spills or wastes, the suppression of vapors is the first concern and the aquatic toxicity to plants, fish, and microorganisms is the second. Normal procedures for flammable liquids should also be carried out.

Even small spills and leaks (<0.45 kg) require extreme caution. Unless the spill is contained in a fume hood, do not remain in or enter the area unless equipped with full protective equipment and clothing. Self-contained breathing apparatus should be used if the odor of acrolein or eye irritation is sensed. Small spills may be covered with absorbant, treated with aqueous alkalies, and flushed with water.

Acrolein is very highly toxic to fish and to the microorganisms in a biological wastewater treatment plant. Avoid drainage to sewers or to natural waters. Safe, practical methods have been devised to handle contained spills of liquid acrolein. These entail covering the acrolein with 15 cm of 3M ATC foam to suppress evaporation followed by either (1) removing some of the foam and igniting the vapors to destroy most of the acrolein under controlled burning conditions, or (2) polymerizing the acrolein by the addition of a dilute (5–10%) aqueous sodium carbonate solution. In situations where the foam covering and controlled burning are not feasible, the acrolein spill may be covered uniformly with dry sodium carbonate amounting to 60–120 kg/m^3 (0.5–1 lb/gal) of acrolein, followed by dilution with 5–10 volumes of water per volume of acrolein. This procedure effectively destroys the acrolein by polymerization but leaves water-insoluble residue. More water (~20 volumes) is needed to get a solution or fine suspension of polymer. Other alkalies, such as dilute aqueous sodium hydroxide, will serve the same purpose but the polymerization is more violent than when the sodium carbonate is used.

8. Government Regulations

The Environmental Protection Agency (EPA) Risk Management Program (RMP), rule 40 CFR 68 lists acrolein as a toxic substance. Chemical processes containing acrolein in quantities of 5000 lb or more are subject to the RMP rule. The rule was promulgated to facilitate prevention and response planning for releases of

extremely hazardous substances to the air and communication of these plans to the public. The rule strongly emphasizes prevention measures to minimize the consequences of a release to the surrounding community and environment.

OSHA Process Safety Management (PSM) rule 29 CFR 1910.119 lists acrolein as a toxic substance. Chemical processes containing acrolein quantities of 150 lb or more are subject to the rule. The purpose of the rule is to protect employees inside the workplace from process safety hazard.

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) requires notification to the National Response Center of releases of quantities of hazardous substances equal to or greater than the reportable quantity (RQ) in 40 CFR 302.4. The reportable quantity for acrolein is 1 lb (0.454 kg).

The Superfund Amendments and Reauthorization Act of 1986 (SARA) Title III requires emergency planning based on threshold planning quantities (TPQ). The TPQ for acrolein is 500 lb (227 kg). SARA also requires submission of annual reports of release of toxic chemicals that appear on the list in 40 CFR 372.65 (for SARA 313). Acrolein appears on that list. This information must be included in all MSDSs that are copied and distributed for acrolein.

The Clean Air Act Amendments of 1990 list acrolein as a hazardous air pollutant. Processes involving acrolein may be subject to emission control requirements.

Acrolein in its "commercial product" (refined) form is a listed RCRA hazardous waste. Refined acrolein and wastes that contain or are derived from "commercial product" acrolein must be managed as RCRA hazardous waste with waste code P003.

Acrolein is a DOT Flammable Liquid having subsidiary DOT hazard classifications of Poison B and Corrosive Material. It is also an inhalation hazard that falls under the special packaging requirements of 49 CFR 173.3a.

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W. G. ETZKORN
S. E. PEDERSEN
T. E. SNEAD
The Dow Company