Kirk-Othmer Encyclopedia of Chemical Technology.

CYANOHYDRINS

A cyanohydrin is an organic compound that contains both a cyanide and a hydroxy group on an aliphatic section of the molecule. Cyanohydrins are usually α-hydroxy nitriles which are the products of base-catalyzed addition of hydrogen cyanide to the carbonyl group of aldehydes and ketones. The IUPAC name for cyanohydrins is based on the α-hydroxy nitrile name. Common names of cyanohydrins are derived from the aldehyde or ketone from which they are formed (Table 1).

The outstanding chemical property of cyanohydrins is the ready conversion to α-hydroxy acids and derivatives, especially α-amino and α,β-unsaturated acids. Because cyanohydrins are primarily used as chemical intermediates, data on production and prices are not usually published. The industrial significance of cyanohydrins is waning as more direct and efficient routes to the desired products are developed. Acetone cyanohydrin is the world's most prominent industrial cyanohydrin because it offers the main route to methyl methacrylate manufacture.

1. Physical Properties

Cyanohydrins are usually colorless to straw yellow liquids with an objectionable odor akin to that of hydrogen cyanide. The lower molecular-weight cyanohydrins can be distilled under reduced pressure provided the cyanohydrin is kept at a slightly acidic pH. Table 2 lists physical properties of some common cyanohydrins.

2. Chemical Properties

Cyanohydrins can react either at the nitrile group or at the hydroxyl group.

2.1. Nitrile Group

Hydrolysis of the nitrile group proceeds through the amide to the corresponding carboxylic acid. Because cyanohydrins are unstable at high pH, this hydrolysis must be catalyzed by acids. In cases where amide hydrolysis is slower than nitrile hydrolysis, the amide may be isolated.

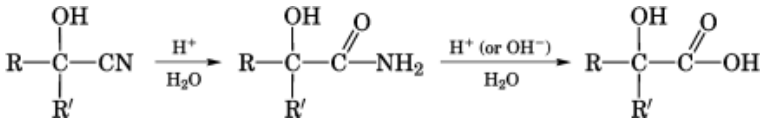
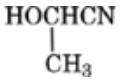
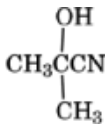
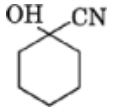
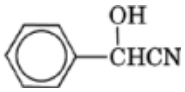
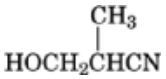


Table 1. Cyanohydrin Nomenclature

Name	CAS Registry Number	Formula	Synonyms
hydroxyacetonitrile	[107-16-4]	$HOCH_2CN$	formaldehyde cyanohydrin, glycolonitrile
2-hydroxypropanenitrile	[78-97-7]		acetaldehyde cyanohydrin, lactonitrile
2-hydroxy-2-methylpropanenitrile	[75-86-5]		acetone cyanohydrin, α-hydroxyisobutyronitrile, 2-methyllactonitrile
1-hydroxy-cyclohexanecarbonitrile	[931-97-5]		cyclohexanone cyanohydrin
α-hydroxy-benzeneacetonitrile	[532-28-5]		benzaldehyde cyanohydrin, mandelonitrile
3-hydroxypropanenitrile[a]	[109-78-4]	$HOCH_2CH_2CN$	ethylene cyanohydrin, hydracrylonitrile
3-hydroxy-2-methylpropanenitrile[a]	[2567-01-3]		propylene cyanohydrin, 2-methylhydraacrylonitrile

[a] A β-hydroxy nitrile.

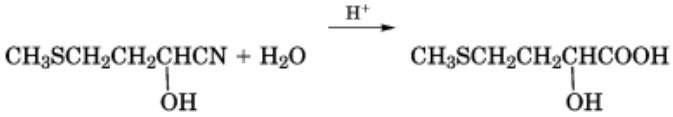
Table 2. Physical Properties of Some Cyanohydrins

Name	Mol wt	Mp, °C	Bp,[a] °C	Specific gravity	n_D^{20}	Flash point, °C
formaldehyde cyanohydrin	57.06	< -72	119 at 3.2 kPa[b]	1.104	1.4117	
acetaldehyde cyanohydrin	71.03	−40	182–184, dec	0.988	1.4050	77
acetone cyanohydrin	85.10	−19	85 at 3.1 kPa[b]	0.927	1.3992	74
cyclohexanone cyanohydrin	121.17	29	109–113 at 1.2 kPa[b]	1.032	1.4576	60
benzaldehyde cyanohydrin	133.15	−10	170, dec	1.117	1.5315	
ethylene cyanohydrin	71.08	−46.2	228	1.059	1.4256	129
propylene cyanohydrin	85.11		207		1.4280	

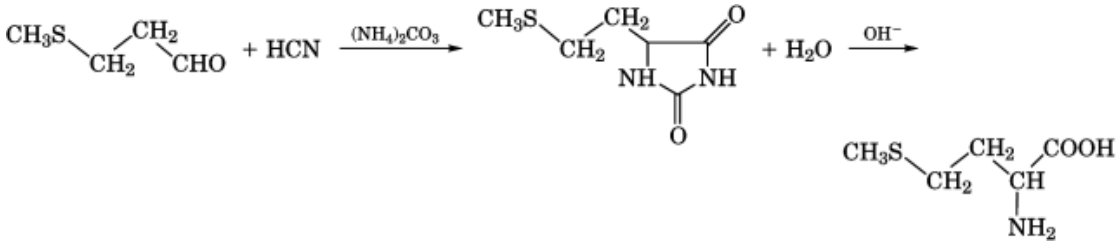
[a] At 101.1 kPa[b] unless otherwise noted.
[b] To convert kPa to mm Hg, multiply by 7.5.

Thus acid hydrolysis of acetophenone cyanohydrin [20102-12-9] ($R = C_6H_5$, $R' = CH_3$) yields the corresponding amide which can be isolated. Further hydrolysis, usually with sodium hydroxide, gives atrolactic acid [575-30-0] in a 30% overall yield (1).

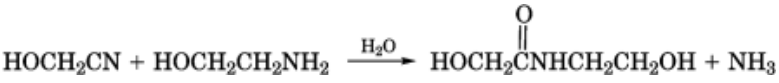
2-Hydroxy-4-methylthiobutyric acid [583-91-5], the hydroxy analogue of the amino acid methionine, is manufactured by acid hydrolysis of 3-methylthiopropionaldehyde cyanohydrin [17773-41-0], which is produced by the reaction of methyl mercaptan with acrolein (qv).



The mixture of D and L optical forms of this hydroxy analogue of methionine is converted to the calcium salt which is used in animal feed supplements. Cyanohydrins react with ammonium carbonate to form hydantoins (2), which yield amino acids upon hydrolysis. Commercial DL-methionine [59-57-8] is produced by hydrolysis of the hydantoin of 3-methylthiopropionaldehyde [3268-49-3].



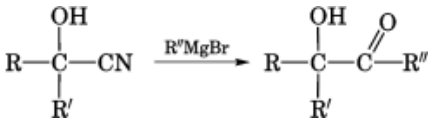
Reaction of cyanohydrins with absolute ethanol in the presence of HCl yields the ethyl esters of α-hydroxy acids (3). *N*-substituted amides can be synthesized by heating a cyanohydrin and an amine in water. Thus formaldehyde cyanohydrin and β-hydroxyethylamine lead to *N*-(β-hydroxyethyl)hydroxyacetamide (4).



Catalytic hydrogenation of the nitrile function of cyanohydrins can give amines. As in the case of ordinary nitriles, catalytic reduction of cyanohydrins can yield a mixture of primary, secondary, and tertiary amines. Addition of acid or acetic anhydride to the reaction medium minimizes formation of secondary or tertiary amines through formation of the amine salt or acetamide derivative of the primary amine.

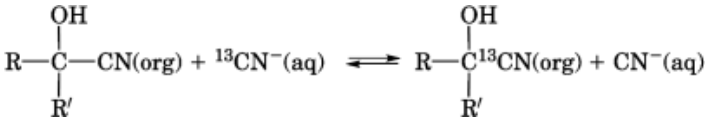
High yields of optically active cyanohydrins have been prepared from hydrogen cyanide and carbonyl compounds using an enzyme as catalyst. Reduction of these optically active cyanohydrins with lithium aluminum hydride in ether affords the corresponding substituted, optically active ethanolamine (5) (see Alkanolamines).

Addition of hydrogen cyanide to an aldose to form a cyanohydrin is the first step in the Kiliani-Fischer method for increasing the carbon chain of aldoses by one unit. Cyanohydrins react with Grignard reagents (see Grignard reaction) to give α-hydroxy ketones.



2.1.1. Cyanide Exchange

Acetone cyanohydrin and methyl isobutyl ketone cyanohydrin [4131-68-4] dissolved in an organic solvent, such as diethyl ether or methyl isobutyl ketone, undergo cyanide exchange with aqueous cyanide ion to yield a significant cyanide carbon isotope separation. The two-phase system yields cyanohydrin enriched in carbon-13 and aqueous cyanide depleted in carbon-13. Equilibrium is obtained in seconds.



Some nitrogen isotope separation is also observed (6).

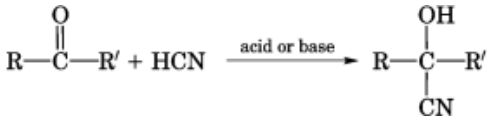
2.2. Hydroxyl Group

The OH group of cyanohydrins is subject to displacement with other electronegative groups. Cyanohydrins react with ammonia to yield amino nitriles. This is a step in the Strecker synthesis of amino acids. A one-step synthesis of α-amino acids involves treatment of cyanohydrins with ammonia and ammonium carbonate under pressure. Thus acetone cyanohydrin, when heated at 160°C with ammonia and ammonium carbonate for 6 h, gives α-aminoisobutyric acid [62-57-7] in 86% yield (7). Primary and secondary amines can also be used to displace the hydroxyl group to obtain *N*-substituted and *N,N*-disubstituted α-amino nitriles. The Strecker synthesis can also be applied to aromatic ketones. Similarly, hydrazine reacts with two molecules of cyanohydrin to give the disubstituted hydrazine.

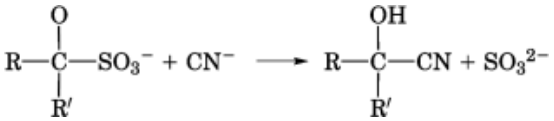
Cyanohydrins react with hydrogen halides or PCl_5 to give α-halo nitriles which can be further hydrolyzed to the α-halo carboxylic acids. The α-hydroxy group of cyanohydrins can be esterified with an acid or acid chloride. Dehydration of cyanohydrins with phosphorus pentoxide gives >80% yields of alkylacrylonitriles (8).

3. Preparation

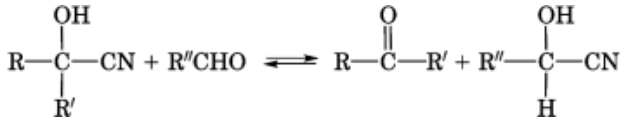
Cyanohydrins can be formed by (*1*) the acid- or base-catalyzed reaction of hydrogen cyanide with an aldehyde or ketone:



(*2*) the displacement of bisulfite ion by cyanide ion on the bisulfite addition compounds of aldehydes and ketones:

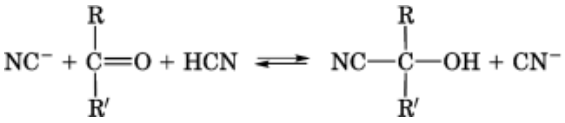


or (*3*) the exchange of cyanide ion between a ketone cyanohydrin and an aldehyde to give the usually more stable aldehyde cyanohydrin:



Direct combination of hydrogen cyanide and a carbonyl compound is the commercial and most common route to cyanohydrins.

The base-catalyzed addition of hydrogen cyanide to carbonyl compounds was one of the first mechanistic studies in organic chemistry (9). Addition of the cyanide ion to the carbonyl group is the rate controlling step. The reaction is slightly subject to general acid catalysis (10, 11), an observation common to many other nucleophilic additions to carbonyl groups. Cyanohydrin formation probably proceeds by attack of cyanide ion on a carbonyl group that is already hydrogen bonded to a proton donor, ie, hydrogen cyanide (12).



The reaction is exothermic and reversible. Stabilization of the product mixture with acid is necessary before the cyanohydrin can be isolated, usually by distillation at reduced pressure.

All aliphatic aldehydes and most ketones react to form cyanohydrins. The lower reactivity of ketones, relative to aldehydes, is attributed to a combination of electron-donating effects and increased steric hindrance of the second alkyl group in the ketones. The magnitude of the equilibrium constants for the addition of hydrogen cyanide to a carbonyl group is a measure of the stability of the cyanohydrin relative to the carbonyl compound plus hydrogen cyanide:

$$K = \frac{[cyanohydrin]}{[HCN]\ \ [carbonylcompound]}$$

The large values of the equilibrium constants for the aldehydes listed in Table 3 indicate the ease of forming aldehyde cyanohydrins relative to the majority of the ketone cyanohydrins. The most sterically hindered ketones, diisopropyl ketone and isopropyl *t*-butyl ketone, do not form appreciable amounts of cyanohydrins. Electron-deficient groups, which stabilize the electron-deficient carbonyl carbon atom, decrease *K*. Aromatic aldehydes form cyanohydrins, but an excess of aromatic aldehyde in basic cyanide solution can lead to further reaction to give benzoin condensation products. Alkyl aryl ketones can form cyanohydrins to a limited extent although the equilibrium usually falls far on the side of the reactants, ketone plus hydrogen cyanide. Diaryl ketones do not form cyanohydrins by this route. Alkyl aryl ketones can be converted to cyanohydrins by treatment with either diethyl aluminum cyanide (15), or by treating with $(CH_3)_3SiCN$ followed by 3*N* HCl (16). The large cyanohydrin formation constants of some cyclohexanones listed in Table 3 are attributed to a reduction of steric strain of the six-membered ring of the cyanohydrin relative to that of the ketone (13). The stability of cyclohexanone cyanohydrin is such that treatment of the cyanohydrin with potassium hydroxide does not give HCN and ketone, but yields instead the potassium salt of the cyanohydrin.

Production of cyanohydrins is accomplished through the base-catalyzed combination of hydrogen cyanide and the carbonyl compound in a solvent, usually the cyanohydrin itself (17). The reaction is carried out at high dilution of the feeds, at 10–15°C, and pH 6.5–7.5. The product is continuously removed from the reaction zone, cooled to push the equilibrium toward cyanohydrin formation, and then stabilized with mineral acid. Purification is usually effected by distillation.

Table 3. Equilibrium Constants for Formation of Cyanohydrins from Hydrogen Cyanide Plus Carbonyl Compounds[a]

Carbonyl compound	K, M^{-1}[b]	References
acetaldehyde	7100	13
propionaldehyde	476	14
n-butyraldehyde	1042	14
isobutyraldehyde	1042	14
acetone	28	13
methyl ethyl ketone	33	13
methyl isopropyl ketone	52	13
methyl *t*-butyl ketone	29	13
isopropyl *t*-butyl ketone	0.12	13
methyl cyclohexyl ketone	56	13
cyclobutanone	108	13
cyclopentanone	34	13
cyclohexanone	1700	13
2-methylcyclohexanone	930	13
2-*t*-butylcyclohexanone	7.6	13
4-*t*-butylcyclohexanone	1700	13
cycloheptanone	7.7	14
benzaldehyde	200	13
p-chlorobenzaldehyde	204	14
p-nitrobenzaldehyde	55	14
p-methoxybenzaldehyde	32	14
m-chlorobenzaldehyde	400	14
m-nitrobenzaldehyde	370	14
m-methoxybenzaldehyde	233	14
o-chlorobenzaldehyde	1000	14
o-nitrobenzaldehyde	1429	14
o-methoxybenzaldehyde	385	14
acetophenone	0.8	14
ethyl phenyl ketone	1.7	14
n-propyl phenyl ketone	1.1	14
isopropyl phenyl ketone	4.0	14
isobutyl phenyl ketone	0.6	14
t-butyl phenyl ketone	11.1	14

[a] Equilibrium constants measured at 20–25°C, except isopropyl *t*-butyl ketone which was measured at 35°C.
[b] Reciprocal molarity or L/mol.

4. Shipping, Storage, and Handling

Cyanohydrins should be stabilized with acid to pH 3–4 to prevent decomposition to hydrogen cyanide and carbonyl compound (18). Formaldehyde cyanohydrin should be considered an explosion and fire risk, particularly if impure. Acetone cyanohydrin and lactonitrile are usually manufactured and used at the same site without shipping. When shipped, steel drums, carboys, tank cars, and barges are used (19). In general, cyanohydrins are combustible liquids and many decompose upon heating. They should be stored in a cool, dry place preferably outside and separated from other storage. Containers should be protected against physical damage (19, 20).

5. Health and Safety

Cyanohydrins are highly toxic by inhalation or ingestion, and moderately toxic through skin absorption (21). All α-hydroxy nitriles are potential sources of hydrogen cyanide or cyanides and must be handled with considerable caution. Contact with the skin and inhalation should be rigorously avoided. Special protective clothing should be worn and any exposure should be avoided (18, 20). The area should be adequately ventilated. Immediate medical attention is essential in case of cyanohydrin poisoning.

6. Uses

Cyanohydrins are used primarily as intermediates in the production of other chemicals. Manufacture of methyl methacrylate, used to make acrylic molding resins and clear sheet, eg, Plexiglas acrylic sheet, from acetone cyanohydrin is the most economically important cyanohydrin process (see Methacrylic polymers). Cyanohydrins are also used as solvents in applications including fiber-spinning and metals refining. Cyanohydrins and derivatives reportedly act as antiknock agents in fuel oil and motor fuels and serve as electrolytes in electrolytic capacitors.

7. Specific Compounds

7.1. Formaldehyde Cyanohydrin

This cyanohydrin, also known as glycolonitrile [107-16-4], is a colorless liquid with a cyanide odor. It is soluble in water, alcohol, and diethyl ether. Equimolar amounts of 37% formaldehyde and aqueous hydrogen cyanide mixed with a sodium hydroxide catalyst at 2°C for one hour give formaldehyde cyanohydrin in 79.5% yield (22).

Although usually handled as an aqueous solution, formaldehyde cyanohydrin can be isolated in the anhydrous form by ether extraction, followed by drying and vacuum distillation (23). Pure formaldehyde cyanohydrin tends to be unstable especially at high pH. Small amounts of phosphoric acid or monochloroacetic acid are usually added as a stabilizer. Monochloroacetic acid is especially suited to this purpose because it codistills with formaldehyde cyanohydrin (24). Properly purified formaldehyde cyanohydrin has excellent stability (25).

Direct reaction of formaldehyde cyanohydrin and ethylenediamine in the presence of a sulfuric acid catalyst gives ethylenediaminetetraacetonitrile [5766-67-6], hydrolysis of which leads to ethylenediaminetetraacetic acid [60-00-4] (EDTA), a widely used sequestering agent (26).

$$HOCH_2CN + H_2NCH_2CH_2NH_2 \longrightarrow (NCCH_2)_2NCH_2CH_2N(CH_2CN)_2 \xrightarrow{H_2O}$$

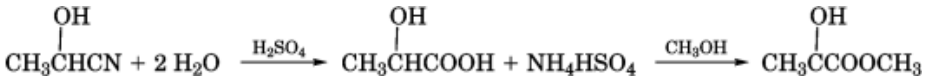
$$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$$

Nitrilotriacetonitrile [628-87-5], $N(CH_2CN)_3$, a precursor to nitrilotriacetic acid [139-13-9], $N(CH_2COOH)_3$, can be prepared from the reaction of formaldehyde cyanohydrin with ammonia (26). Formaldehyde cyanohydrin is also used as an intermediate in pharmaceutical production. Commercial formaldehyde cyanohydrin is available as a 70% aqueous solution stabilized by phosphoric acid.

Formaldehyde cyanohydrin was detected in Halley's comet by the Vega I space probe (27).

7.2. Acetaldehyde Cyanohydrin

This cyanohydrin, commonly known as lactonitrile, is soluble in water and alcohol, but insoluble in diethyl ether and carbon disulfide. Lactonitrile is used chiefly to manufacture lactic acid and its derivatives, primarily ethyl lactate. Lactonitrile [78-97-7] is manufactured from equimolar amounts of acetaldehyde and hydrogen cyanide containing 1.5% of 20% NaOH at $-10 - 20\ ^{\circ}C$. The product is stabilized with sulfuric acid (28). Sulfuric acid hydrolyzes the nitrile to give a mixture of lactic acid [598-82-3] and ammonium bisulfate.



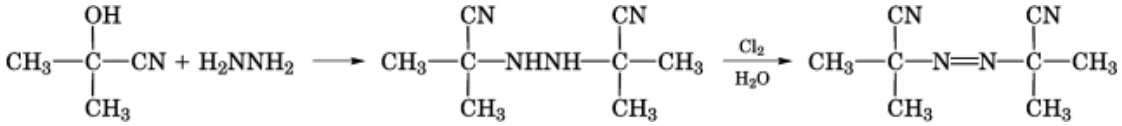
This mixture can be purified by adding methanol to form methyl lactate [547-64-8] which is separated from the ammonium bisulfate. The methyl lactate is distilled, then hydrolyzed back to the aqueous acid. Removal of most of the water yields 90% lactic acid (29).

7.3. Acetone Cyanohydrin

This cyanohydrin, also known as α-hydroxyisobutyronitrile and 2-methyllactonitrile [75-86-5], is very soluble in water, diethyl ether, and alcohol, but only slightly soluble in carbon disulfide or petroleum ether. Acetone cyanohydrin is the most important commercial cyanohydrin as it offers the principal commercial route to methacrylic acid and its derivatives, mainly methyl methacrylate [80-62-6] (see Methacrylic acid and derivatives). The principal U.S. manufacturers are Rohm and Haas Co., Du Pont, CyRo Industries, and BP Chemicals. Production of acetone cyanohydrin in 1989 was 582,000 metric tons (30).

Acetone cyanohydrin is used as a raw material for insecticides manufacture and also to produce ethyl α-hydroxyisobutryate [80-55-7], a pharmaceutical intermediate. It has been used as a complexing agent for metals refining and separation. Acetone cyanohydrin complexes can be used to separate Ni^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, or Fe^{2+} from Mg^{2+}, Ba^{2+}, Ca^{2+}, Na^{+}, or K^{+} on strongly basic ion-exchange resins (31). Acetone cyanohydrin is also used as a reagent in the formation of aldehyde cyanohydrins from aldehydes; in combination with a KCN-crown ether complex, it acts as an effective, stereoselective hydrocyanating reagent (32).

Reaction of hydrazine with acetone cyanohydrin gives a disubstituted hydrazine, which upon oxidation with chlorine water gives 2,2′-azobisisobutyronitrile [78-67-1] (AIBN), a stable, colorless, crystalline material at room temperature.



When heated to 120°C, AIBN decomposes to form nitrogen and two 2-cyanoisopropyl radicals. The ease with which AIBN forms radicals, and the fact that the rate of information does not vary much in various solvents has resulted in wide use of AIBN as a free-radical initiator. AIBN is used commercially as a catalyst for vinyl polymerization (see Initiators).

Acetone cyanohydrin is manufactured (33) by the direct reaction of hydrogen cyanide with acetone, catalyzed by base, generally in a continuous process (Fig. 1). Acetone and hydrogen cyanide are fed continuously with a small amount of sodium hydroxide catalyst to the stirred acetone cyanohydrin generator. Since the reaction is exothermic, acetone cyanohydrin is also used as the reaction solvent to aid in dissipating the heat of reaction. To push the equilibrium toward cyanohydrin formation, the reaction mixture is chilled first in the generator, then in the hold tank. The crude acetone cyanohydrin is neutralized with sulfuric acid to pH

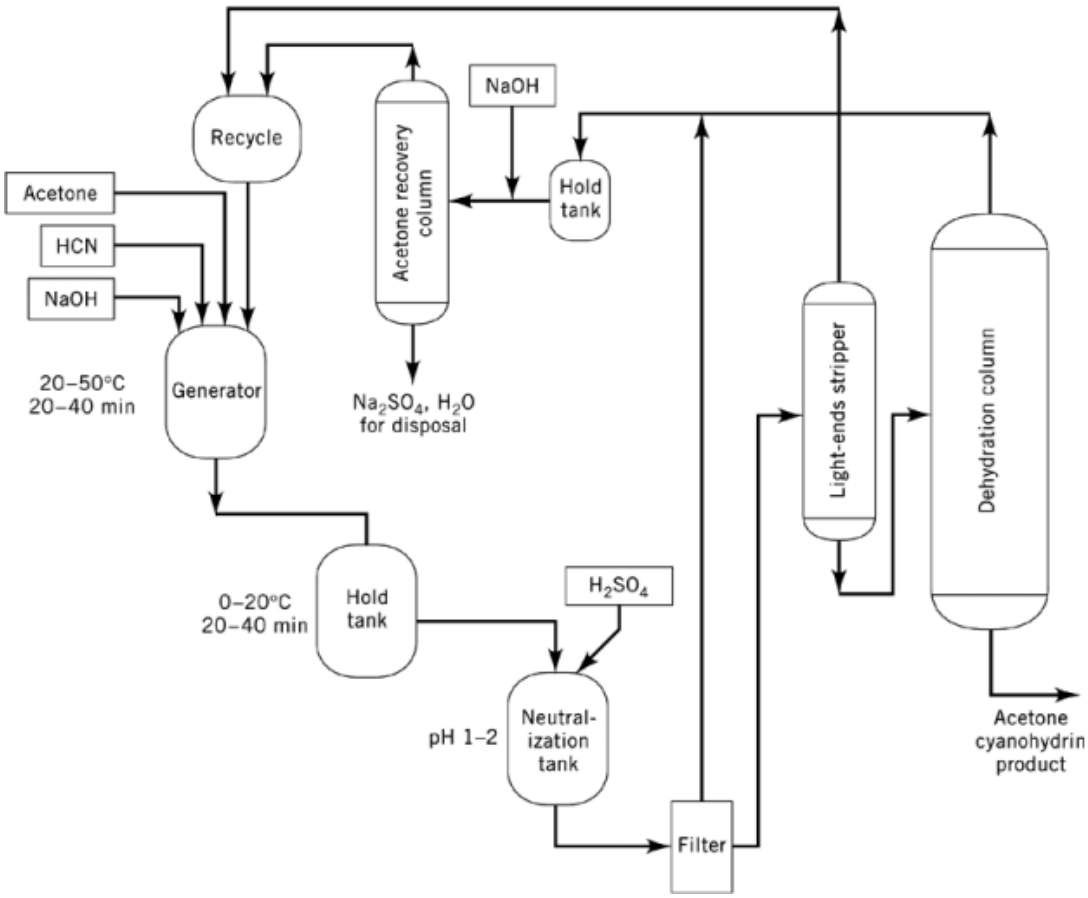


Fig. 1. Acetone cyanohydrin process.

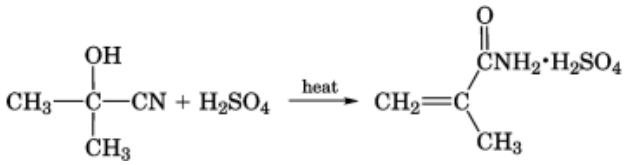
1–2 (19). The acidification causes precipitation of the sodium catalyst as sodium sulfate salts which are then filtered. The crude acetone cyanohydrin is fed to a light-ends stripping column where the hydrogen cyanide, acetone, and some of the water are removed overhead and recycled to the acetone cyanohydrin generator. The concentrated acetone cyanohydrin bottoms are then sent to a dehydration column where the remainder of the water is removed under vacuum. The anhydrous acetone cyanohydrin is removed as the bottoms product and used directly in methacrylate manufacture.

Single-pass conversions of acetone cyanohydrin are 90–95% depending on the residence times and temperatures in the generator and hold tank. Overall yields of product from acetone and hydrogen cyanide can be $>$97%. There are no significant by-products of the reaction other than the sodium salts produced by neutralization of the catalyst.

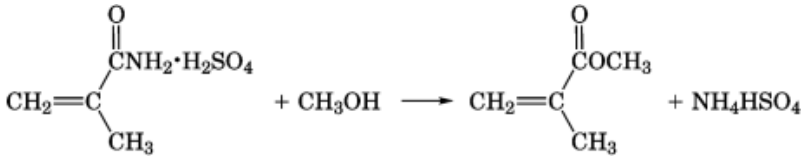
The hydrogen cyanide used in the process is sometimes produced on-site through catalytic conversion of an ammonia-methane-air mixture directly to hydrogen cyanide, the Andrussow process. However, by-product hydrogen cyanide from acrylonitrile (qv) manufacture is increasingly being used in acetone cyanohydrin production. Although sodium hydroxide was used as the catalyst in the above example, any of a number of other basic catalysts would suffice including KOH, K_2CO_3 (18), ion-exchange resins (34), and acetic acid-sodium acetate buffers (35).

10 CYANOHYDRINS

Acetone cyanohydrin is used for methacrylate manufacture. Sulfuric acid is added in greater than an equimolar amount, and by thermal cracking the acetone cyanohydrin is converted to methacrylamide sulfate [29194-31-8].

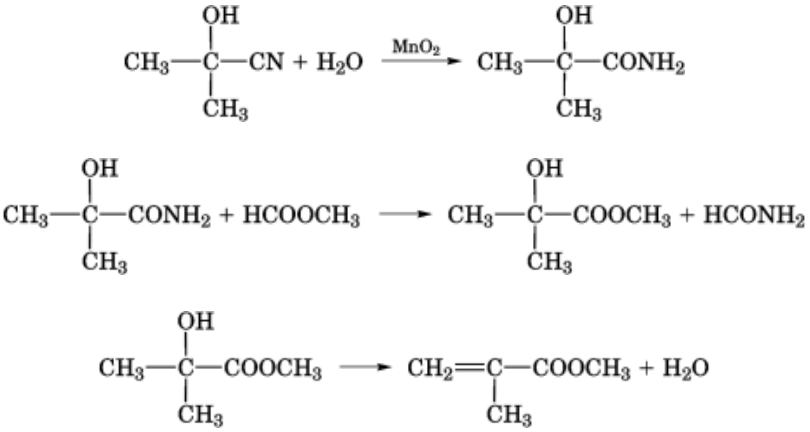


The methacrylamide sulfate is esterified with methanol to give methyl methacrylate and ammonium bisulfate [7802-63-6] as a by-product.



The basic process for manufacture of acetone cyanohydrin was developed in the 1930s by Imperial Chemical Industries and has been improved over the years by the producing companies.

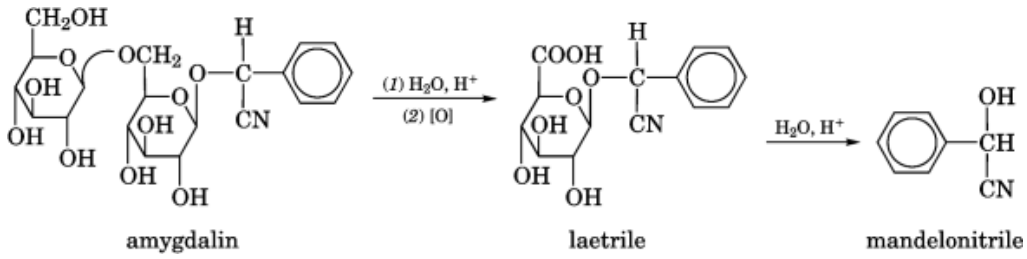
Conversion of acetone cyanohydrin to methyl methacrylate produces a large amount of ammonium bisulfate by-product which lacks ready marketability and is usually converted to sulfuric acid for reuse in the conversion of acetone cyanohydrin to methacrylates. The nitrogen values of the ammonium bisulfate are lost in the recycle process. The necessity for the ammonium bisulfate recycle plants has created increased interest in routes to methacrylates that do not coproduce ammonium bisulfate (36). Mitsubishi Gas Chemical has developed a new route from acetone cyanohydrin to methyl methacrylate (37) which produces water as a by-product. In this process acetone cyanohydrin (α-hydroxyisobutyronitrile [75-86-5]) is hydrated to yield α-hydroxy isobutyramide [13027-88-8]. Ester interchange between α-hydroxy isobutyramide and methyl formate yields methyl α-hydroxy isobutyrate [2110-78-3] which is dehydrated to methyl methacrylate (MMA).



The formamide is dehydrated to HCN which is recycled back to make acetone cyanohydrin. The overall reaction is acetone + methyl formate $\longrightarrow$ MMA + H_2O.

7.4. Benzaldehyde Cyanohydrin

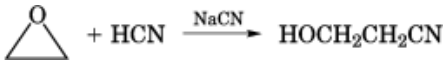
This cyanohydrin, also known as mandelonitrile [532-28-5], is a yellow, oily liquid, insoluble in water, but soluble in alcohol and diethyl ether. Mandelonitrile is a component of the glycoside amygdalin [29883-15-6], a precursor of laetrile [1332-94-7] found in the leaves and seeds on most *Prunus* species (plum, peach, apricot, etc). In 1832, mandelonitrile was the first cyanohydrin to be synthesized.



It is commercially prepared from benzaldehyde and hydrogen cyanide. Mandelonitrile is used by certain insects (tiger beetles, an African millipede) as a defense fluid (38). After expelling the fluid an enzyme catalyzes the conversion of mandelonitrile to benzaldehyde and HCN, which is usually fatal to the insect's enemy.

7.5. Ethylene Cyanohydrin

This cyanohydrin, also known as hydracrylonitrile or glycocyanohydrin [109-78-4],is a straw-colored liquid miscible with water, acetone, methyl ethyl ketone, and ethanol, and is insoluble in benzene, carbon disulfide, and carbon tetrachloride. Ethylene cyanohydrin differs from the other cyanohydrins discussed here in that it is a β-cyanohydrin. It is formed by the reaction of ethylene oxide with hydrogen cyanide.



Like the formation of α-cyanohydrins, this reaction is catalyzed by bases or cyanide ion, but unlike the α-cyanohydrin case this reaction is not reversible, and under certain conditions it can proceed with violence. Ethylene cyanohydrin can also be prepared by the reaction of ethylene chlorohydrin and alkali cyanides (39).

The first U.S. plant for acrylonitrile manufacture used an ethylene cyanohydrin feedstock. This was the primary route for acrylonitrile manufacture until the acetylene-based process began to replace it in 1953 (40). Maximum use of ethylene cyanohydrin to produce acrylonitrile occurred in 1963. Acrylonitrile (qv) has not been produced by this route since 1970.

The first commercial process for manufacture of acrylic acid (qv) and acrylates involved hydrolysis of ethylene cyanohydrin in aqueous sulfuric acid.

$$HOCH_2CH_2CN \xrightarrow{H_2SO_4} CH_2{=}CHCOOH + NH_4HSO_4$$

This route is no longer commercially significant.

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