

PROPERTIES AND USES OF ACRYLIC ACID

Acrylic acid is a colorless liquid with an irritating acrid odor at room temperature and pressure. Its odor threshold is low (0.20-3.14 mg/m³). It is miscible in water and most organic solvents.

Acrylic acid is commercially available in two grades: technical grade (94%) for esterification, and glacial grade (98-99.5% by weight and a maximum of 0.3% water by weight) for production of water-soluble resins. Acrylic acid polymerizes easily when exposed to heat, light or metals, and so a polymerization inhibitor is added to commercial acrylic acid to prevent the strong exothermic polymerization. The inhibitors that are usually used in acrylic acid preparations are the

- monomethyl ether of hydroquinone (methoxyphenol) at 200 ± 20 ppm
- phenothiazine at 0.1%
- hydroquinone at 0.1%
- Methylene blue at 0.5 to 1.0%
- N,N'-diphenyl- p-phenylenediamine at 0.05% can also be used.

Acrylic acid reacts readily with free radicals and electrophilic or nucleophilic agents. It may polymerize in the presence of acids (sulfuric acid, chlorosulfonic acid), alkalis (ammonium hydroxide), amines (ethylenediamine, ethyleneimine, 2-aminoethanol), iron salts, elevated temperature, light, peroxides, and other compounds that form peroxides or free radicals. In the absence of inhibitor, peroxides are formed when oxygen is sparged into acrylic acid. The presence of oxygen is required for the stabilizer to function effectively. Acrylic acid must never be handled under an inert atmosphere.

Freezing of acrylic acid occurs at 13°C. Rethawing under inappropriate temperature conditions is another frequent reason for acrylic acid polymerization.

Acrylic acid is a strong corrosive agent to many metals, such as unalloyed steel, copper and brass.

PHYSICAL CONSTANTS ARE LISTED BELOW

PROPERTY	
Molecular weight	72
Melting point °C	13.5
Density g/ml	1.045 (25°C)
Boiling point °C / mmHg	141/760
Refractive index	1.4185 (25°C)
Flash point (COC), °C	68
Kinematic viscosity, cks, at 25°C	1.1
Dissociation constant at 25°C	5.50×10^{-5}
pK _B	4.26
Solubility at 25°C in water, parts/100	infinity
Critical temperature, °C	380
Critical pressure, MPa	5.06
Heat of vaporization at 101.3 kPa	45.6 kJ/mol
Heat of combustion	1376 kJ/mol
Heat of melting at 13°C	11.1 kJ/mol
Heat of neutralization	58.2 kJ/mol
Heat of polymerisation	77.5 kJ/mol
Autoignition temperature (°C)	390-446
Henry's law constant	$3.2 \times 10^{-7} \text{ atm} \times \text{m}^3/\text{mol}$
Solubility in organic solvents	
alcohol	miscible
chloroform	miscible
benzene	miscible
acetone	soluble (> 10 %)

CHEMICAL PROPERTIES:

Acrylic acid undergo reactions characteristics of both unsaturated acids and aliphatic carboxylic acids or esters. The high reactivity of these compounds stems from the two unsaturated centers situated in the conjugated position. The β carbon atom, polarized by carbonyl group, behaves as an electrophile; this favours the addition of large variety of nucleophiles and active hydrogen compounds to the vinyl group. Moreover, the

carbon-carbon double bond undergoes radical-initiated addition reactions, Diels-Alder reactions with dienes, and polymerization reactions.

The carboxyl function is subject to the displacement reactions typical of aliphatic acids and esters, such as esterification and transesterification.

Joint reactions of the vinyl and carboxyl functions, especially with bifunctional reagents, often constitute convenient route to polycyclic and heterocyclic substances.

Acrylic acids polymerise very easily. The polymerization is catalysed by heat, light, and peroxides and inhibited by stabilizers, such as monomethyle ether of hydroquinone or hydroquinone itself. These phenolic inhibitors are effective only in the presence of oxygen. The highly exothermic, spontaneous polymerization of acrylic acid is extremely violent.

Addition Reactions:

Acrylic acid combine readily with substances such as hydrogen, hydrogen halides and hydrogen cyanides, that customarily add to olefins:



where X=H, halogen or CN.

Michael addition of organic substance take place in the presence of basic catalysts, such as tertiary amines, quaternary ammonium salts, and alkali alkoxides:

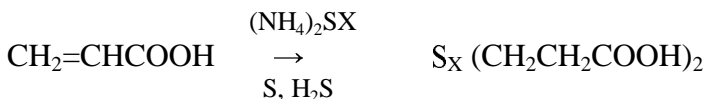
where X = -C(NO₂)R'R'', -CH(COOR')₂ and R', R'' = alkyl or aryl.

Ammonia and amines are sufficiently basic to react without a catalyst :

where X = -NH₂, -NHR', -NR'R'', -NR'COR'' or -NHNR₂.

The addition of aromatic amines or amides and tert- alkly primary amines is more effectively promoted by acids. Amines may attack both the vinyl and carboxyl functions, but the products of such reaction decompose to give N- substituted amides.

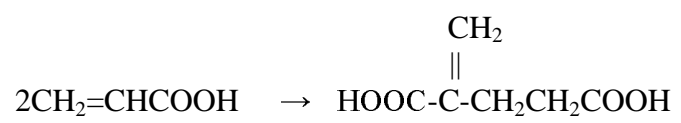
Hydrogen sulfide in the presence of sulfur and ammonium polysulfide or amine catalysts gives polythiodipropionic acids and esters .



At elevated temperature or on longer storage acrylic acid dimerizes:



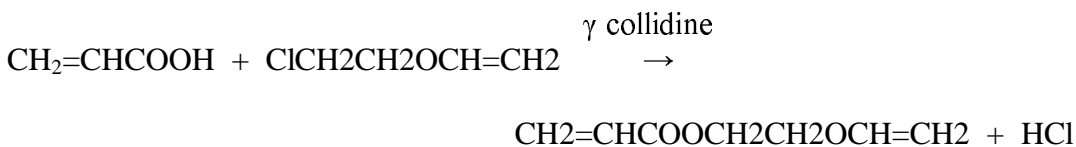
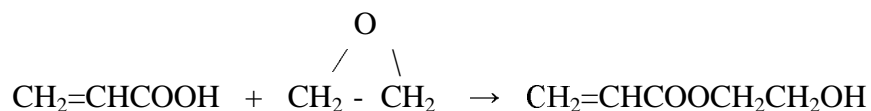
In the presence of catalyst such as tributyl phosphine, acrylates can also dimerizes to give 2- methyleneglutarates.



Reactions of the Carboxyl Group.

Acrylic acid is converted readily into its corresponding salts, into acrylic anhydride by reaction with acetic anhydride, or into acryloyl chloride by reaction with benzoyl or thionyl chloride. The esterification of acrylic acid are economically the most important reactions.

Some other examples are:



USES OF ACRYLIC ACIDS:

The worldwide production of acrylic acid in 1994 was estimated to be approximately 2 million tonnes. Acrylic acid is used primarily as a starting material in the production of acrylic esters; as a monomer for polyacrylic acid and salts, as a comonomer with acrylamide for polymers used as flocculants, with ethylene for ion exchange resin polymers, with methyl ester for polymers.

Acrylic acid is used in the field of application of

- plastics
- paper manufacture and coating
- exterior house paints for wood and masonry
- coatings for compressed board and related building materials
- flocculation of mineral ore fines and waste water, and treatment of sewage
- printing inks
- interior wall paints
- floor polishes
- floor and wall coverings
- industrial primers
- textile sizing, treatment and finishing
- leather impregnation and finishing
- masonry sealers

- lubricating and fuel oil additives
- lacquers for automotive, appliance and furniture finishes
- pharmaceutical binders
- hot metal coatings