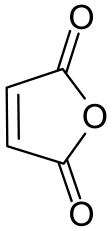
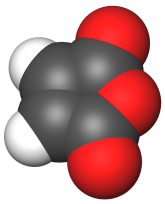
Maleic anhydride

Maleic anhydride[1]	
 	
	
Identifiers	
CAS number	108-31-6 [2] ✓
PubChem	7923 [3]
ChemSpider	7635 [4] ✓
UNII	V5877ZJZ25 [5] ✓
EC-number	203-571-6 [6]
ChEBI	CHEBI:474859 [7] ✗
ChEMBL	CHEMBL374159 [8] ✓
RTECS number	UE5950000
Jmol-3D images	Image 1 [9]
Properties	
Molecular formula	$C_4H_2O_3$
Molar mass	98.06 g/mol
Appearance	White crystals
Density	1.48 g/cm^3
Melting point	52.8 °C (127.0 °F; 325.9 K)
Boiling point	202 °C (396 °F; 475 K)
Solubility in water	Reacts
Hazards	

MSDS	MSDS at J. T. Baker [10]
EU classification	Corrosive (**C**)
R-phrases	R22, R34, R42/43
S-phrases	(S2), S22, S26, S36/37/39, S45
NFPA 704	
Flash point	102 °C (216 °F; 375 K)
Related compounds	
Related acid anhydrides	Succinic anhydride
Related compounds	Maleic acid
Except where noted otherwise, data are given for materials in their standard state (at 25 °C (77 °F), 100 kPa)	
✗ (verify) [11] (what is: ✓ / ✗ ?)	
Infobox references	

Maleic anhydride is an organic compound with the formula $C_2H_2(CO)_2O$. It is the acid anhydride of maleic acid. it is a colourless or white solid with an acrid odour. It is produced industrially on a large scale for applications in coatings and polymers.

Production

Maleic anhydride was traditionally produced by the oxidation of benzene or other aromatic compounds. As of 2006, only a few smaller plants continue to use benzene. Instead, most maleic anhydride plants is produced by vapor-phase oxidation of n-butane. The overall process converts the methyl groups to carboxylate and dehydrogenates the backbone. The selectivity of the process reflects the robustness of maleic anhydride, with its conjugated double-bond system.

In both cases, benzene and butane are fed into a stream of hot air, and the mixture is passed through a catalyst bed at high temperature. The ratio of air to hydrocarbon is controlled to prevent the mixture from igniting. Vanadium pentoxide and molybdenum trioxide are the catalysts used for the benzene route, whereas vanadyl phosphate is used for the butane route.

$$C_4H_{10} + 3.5\ O_2 \rightarrow C_2H_2C_2O_3 + 4\ H_2O\ \Delta H = -1236\ \text{kJ/mol}$$

The main competing process entails full combustion of the butane, a conversion that is twice as exothermic as the partial oxidation.

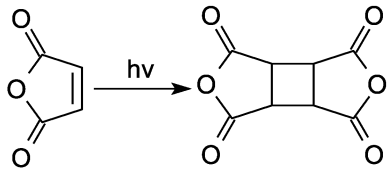
Industrial production of maleic anhydride is achieved by integration of following unit processes: catalyst packed bed reactor, adsorption tower, maleic acid reactor, distillation column. The reactant stream of n-butane and air mixture enters the packed bed reactor at a temperature of 120-150 ºC and a pressure of 2-3 atm. The product stream is then sent to a packed bed adsorption column, where the condensable maleic anhydride reacts with the water stream to give maleic acid and the non-condensable are sent for fuel gases treatment. The condensable stream from adsorption tower is sent to a maleic acid reactor, where maleic acid is again converted back to the anhydride. This product stream from reactor is sent to distillation column to obtain pure maleic anhydride as product.

Reactions

The chemistry of maleic anhydride is very rich, reflecting its ready availability and bifunctional reactivity. It hydrolyzes, producing maleic acid, *cis*-HOOC–CH=CH–COOH. With alcohols, the half-ester is generated, e.g., *cis*-HOOC–CH=CH–$COOCH_3$.

Maleic anhydride is a classic substrate for Diels-Alder reactions.[12] It was used for work in 1928 on the reaction between maleic anhydride and 1,4-butadiene that Diels and Alder were awarded the Nobel prize in 1950. It is through this reaction that maleic anhydride converted to many pesticides and pharmaceuticals.

Maleic anhydride dimerizes in a photochemical reaction to form cyclobutane tetracarboxylic dianhydride (CBTA). This compound is used in the production of polyimides and as an alignment film for liquid crystal displays.<



It is also a ligand for low-valent metal complexes, examples being $Pt(PPh_3)_2$(MA) and $Fe(CO)_4$(MA).

Uses

Around 50% of world maleic anhydride (MA) output is used in the manufacture of unsaturated polyester resins (UPR). Chopped glass fibres are added to UPR to produce fibreglass reinforced plastics which are used in a wide range of applications such as pleasure boats, bathroom fixtures, automobiles, tanks and pipes. However, the UPR market reflects general economic conditions as it is tied to the construction, automobile and marine industries.

The production of 1,4-butandiol (BDO) is also having an impact on the MA market. BDO is one of the world's fastest growing chemicals used in the production of thermoplastic polyurethanes, elastane/Spandex fibres, polybutylene terephthalate (PBT) resins and many other products. However, BDO is made from a crude MA which is not traded and only used for this application.

Another market for MA is lubricating oil additives, which are used in gasoline and diesel engine crankcase oils as dispersants and corrosion inhibitors. Changes in lubricant specifications and more efficient engines have had a negative effect on the demand for lubricating oil additives, giving flat growth prospects for MA in this application.

There are a number of smaller applications for MA. The food industry uses MA in artificial sweeteners and flavour enhancements. Personal care products consuming MA include hair sprays, adhesives and floor polishes. MA is also used in water treatment chemicals, detergents, insecticides and fungicides, pharmaceuticals and copolymers.

Major producers

Company	Location
Bartek Ingredients Inc.	Canada
Sasol-Huntsman	Germany
DSM NV	The Netherlands
Flint Hills Resources LP	USA
Huntsman Corporation	USA
Huntsman Performance Products	USA
Lanxess Corporation	USA
Lonza Group AG	Switzerland
Marathon Petroleum Company LLC	USA
Mitsubishi Chemical Corporation	Japan
Mitsui Chemicals, Inc	Japan
Mitsui Chemicals Polyurethanes, Inc.	Japan
Nippon Shokubai Co., Ltd	Japan
NOF Corporation	Japan
Polynt SpA	Italy
Suzhou Synthetic Chemical Co, Ltd.	China
Thirumalai Chemicals Ltd.	India
TCL Industries Malaysia Sdn. Bhd.	Malaysia

***Source**: Kirk & Othmer*

World Maleic Anhydride Capacity By Region

Data in: *kilo tonnes per annum*

Region	2002	2012
North America	235	311
South & Central America	44	41
Western Europe	168	456
Central & Eastern Europe	64	58
Asia	315	483
Africa	10	10
Total	836	1359

***Source**: Kirk & Othmer*

Worldwide demand

In 2007-2013, the average annual MAN market growth rate was 2.8% in the USA and 3.5% in Western Europe, while in Japan it dropped by 1.4%. Global MAN consumption grew by 6-7 % a year to 1.5 million tons in 2013. World MAN consumption is predicted by consultants to grow at around 3% per year up to 2016. Growth will be slower in Western Europe and the US, but higher in Central and Eastern Europe, Latin America and Asia, in particular China. According to CMR, demand in the US increased from 254,000 tons in 2009 to 281,000 tons in 2013. Growth in Central and South America is expected to be higher than North America at around 4% per year. In

Western Europe, the MAN market is mature with growth predicted around 1.5-2 % per year, while in Central and Eastern Europe growth is much stronger at 4% per year. In Asia, China is the most important MAN market. According to China Chemical Reporter, China produced 236,000-tons in 2008, while it consumed 229,700-tons in the same year. Overall demand is expected to reach 394,000-tons by 2014. China produced around 800,000 tons of UPR during 2008, requiring around 160,000 tons of MAN. In 2014, China expects to produce 1.4 million tons of UPR with demand for MAN rising to about 280,000 tons in this application.

Packing and transport

Liquid maleic anhydride is available in road tankers and/or tank-containers which are made of stainless steel, which are insulated and provided with heating systems to maintain the temperature of 65-75°C. Tank cars must be approved for the transport of molten maleic anhydride.

Liquid/molten maleic anhydride is a dangerous material in accordance with RID/ADR.

Storage

- Requirements for storage buildings
  - Local exhaust systems to take vapours away from the places of emission, and general ventilation in rooms.
  - Protection against static charges.
  - Impervious floor which makes it possible to collect the spilled material and which prevents its entry to the sewage system.
  - Storage rooms should be cool and dry.
- Storage conditions
  - Keep ignition sources away - do not smoke. Product dust may form explosive air-dust mixtures.
  - Keep humidity away from storage rooms.
  - Keep containers tightly closed. Store them in cool, dry and well ventilated places.
  - Tanks / containers must be properly marked.
  - Hand-operated / portable fire-fighting equipment should be available in storage rooms.
  - Neutral gas blanketing is required inside storage tanks.

Effects on human health and the environment

This compound also poses relatively low-risk environmental hazards, an important feature for those applications. Exposure to maleic anhydride may cause respiratory tract, eye irritation, skin irritation and respiratory irritation. Maleic anhydride is a skin - and possibly respiratory – sensitizer.

Maleic anhydride is a low hazard profile chemical. Maleic anhydride rapidly hydrolyzes to form maleic acid in the presence of water and hence environmental exposures to maleic anhydride are not expected to occur. Maleic anhydride and maleic acid are biodegraded under aerobic conditions in sewage sludge and in soil and water as well.

Food starch for use in night markets sold from a supplier in Tainan city, Taiwan, were found to contain maleic anhydride in December 2013. The supplier was investigated regarding the 300 tons of tainted starch; an earlier inspection in November had found 32 tons.[13]

References

[1] *Merck Index*, 11th Edition, **5586**.
[2] http://www.commonchemistry.org/ChemicalDetail.aspx?ref=108-31-6
[3] http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=7923
[4] http://www.chemspider.com/Chemical-Structure.7635.html
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[10] http://hazard.com/msds/mf/baker/baker/files/m0364.htm
[11] http://en.wikipedia.org/w/index.php?title=Special:ComparePages&rev1=409750643&page2=Maleic+anhydride
[12] Samuel Danishefsky, Takeshi Kitahara, and Paul F. Schuda "Preparation and Diels-Alder Reaction of a Highly Nucleophilic Diene: trans-1-Methoxyl-3-Trimethylsiloxy-1,3-Butadiene and 5β-Methoxycyclohexan-1-one-3β,4β-Dicarboxylic acid Andhydride" Org. Synth. 1983, 61, 147
[13] http://www.wantchinatimes.com/news-subclass-cnt.aspx?id=20131219000005&cid=1103

External links

- International Chemical Safety Card 0799 (http://www.inchem.org/documents/icsc/icsc/eics0799.htm)
- NIOSH Pocket Guide to Chemical Hazards 0376 (http://www.cdc.gov/niosh/npg/npgd0376.html)
- Ironic Mr Fox (http://ironicmrfox.blogspot.ca/2013/09/maleic-anhydride-production.html) Alan Fox's video of the Bartek Ingredients Maleic Anhydride production facility in Stoney Creek, ON CA
- Chronic toxicity summary (http://www.oehha.ca.gov/air/chronic_rels/pdf/maleic.pdf)
- Maleic anhydride at Occupational Safety & Health Administration (http://www.osha.gov/dts/sltc/methods/organic/org086/org086.html)

Appendix

Physical Properties: Melting Point : 51-60 °C(lit.)

Boiling Point : 200 °C(lit.)

Density : 1.48

Vapor density : 3.4 (vs air)

Vapor pressure : 0.16 mm Hg (20 °C)

Freezing Point : 218 °F

Storage Temp. : Store at RT.

Form : powder

Water Solubility : 79 g/100 mL (25 °C)

Sensitive : Moisture Sensitive

Merck : 14,5704

BRN : 106909

Stability: Stable. Combustible. Incompatible with water, strong oxidizing agents, alkali metals, strong bases, amines, most common metals, polymerization catalysts and accelerators.

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