# Hydrazine

Hydrazine	
Hydrazhie H 144.9 pm H 102.1 pm H H	
Identifiers	
CAS number	302-01-2 <sup>[1]</sup> ✓, 7803-57-8 (hydrate)
EC number	206-114-9 <sup>[2]</sup>
UN number	2029 (anhydrous) 2030 (aq. soln., 37–64%) 3293 (aq. soln., <37%)
RTECS number	MU7175000
Properties	
Molecular formula	N <sub>2</sub> H <sub>4</sub>
Molar mass	32.05 g/mol (anhydrous) 50.06 g/mol (hydrate)
Appearance	Colourless liquid
Density	1.0045 g/cm <sup>3</sup> (anhydrous) 1.032 g/cm <sup>3</sup> (hydrate)
Melting point	1 °C (274 K, anhydrous) -51.7 °C (hydrate)
Boiling point	114 °C (387 K), anhydrous 119 °C (hydrate)
Solubility in water	miscible
Acidity (pK <sub>a</sub> )	8.1
Refractive index $(n_D)$	1.46044 (22 °C, anhydrous) <sup>[3]</sup> 1.4284 (hydrate)
Viscosity	0.876 cP (25 °C)
Structure	

Molecular shape	pyramidal at N	
Dipole moment	1.85 D <sup>[4]</sup>	
Hazards		
MSDS	ICSC 0281 <sup>[5]</sup>	
EU Index	007-008-00-3	
EU classification	Carc. Cat. 2 Toxic ( <b>T</b> ) Corrosive ( <b>C</b> ) Dangerous for the environment ( <b>N</b> )	
R-phrases	R45, R10, R23/24/25, R34, R43, R50/53	
S-phrases	\$53, \$45, \$60, \$61	
NFPA 704		
Flash point	52 °C	
Autoignition temperature	24–270 °C (see text)	
Explosive limits	1.8-100%	
LD <sub>50</sub>	59–60 mg/kg (oral in rats, mice) <sup>[6]</sup>	
Related compounds		
Related nitrogen hydrides	Ammonia Hydrazoic acid	
Related compounds	monomethylhydrazine dimethylhydrazine phenylhydrazine	
$\checkmark$ (what is this?) (verify) <sup>[7]</sup> Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)		
Infobox references		

**Hydrazine** is an inorganic chemical compound with the formula  $N_2H_4$ . It is a colourless liquid with an ammonia-like odor and is derived from the same industrial chemistry processes that manufacture ammonia. However, hydrazine has physical properties that are closer to those of water.

Hydrazine is highly toxic and dangerously unstable, and is usually handled while in solution for safety reasons.

Hydrazine is mainly used as a foaming agent in preparing polymer foams, but significant applications also include its uses as a precursor to polymerization catalysts and pharmaceuticals. Additionally, hydrazine is used in various rocket fuels and to prepare the gas precursors used in air bags. Approximately 260,000 tons are manufactured annually.<sup>[8]</sup>

### Molecular structure and properties

Hydrazine can arise via coupling a pair of ammonia molecules by removal of one hydrogen per molecule. Each H<sub>a</sub>N-N subunit is pyramidal in shape. The N-N distance is 1.45 Å (145 pm), and the molecule adopts a gauche conformation.<sup>[9]</sup> The rotational barrier is twice that of ethane. These structural properties resemble those of gaseous hydrogen peroxide, which adopts a "skewed" anticlinal conformation, and also experiences a strong rotational barrier.

Hydrazine has basic (alkali) chemical properties comparable to those of ammonia:

 $N_2H_4 + H_2O \rightarrow [N_2H_5]^+ + OH^-$ with the values:<sup>[10]</sup>

 $K_{h} = 1.3 \text{ x } 10^{-6}$ 

 $pK_a = 8.1$ 

(for ammonia  $K_{h} = 1.78 \times 10^{-5}$ )

Hydrazine can be diprotonated only with difficulty:<sup>[11]</sup>

$$[N_2H_5]^+ + H_2O \rightarrow [N_2H_6]^{2+} + OH^-K_b = 8.4 \times 10^{-10}$$

Recent findings in microbiochemistry have found that hydrazine is the intermediate in the anaerobic ammonium oxidation (anammox) process.<sup>[12]</sup>

# Synthesis and manufacture

Theodor Curtius synthesized free hydrazine for the first time in 1889 via a circuitous route.<sup>[13]</sup>

Hydrazine is produced in the Olin Raschig process from sodium hypochlorite (the active ingredient in many bleaches) and ammonia, a process announced in 1907. This method relies on the reaction of chloramine with ammonia.<sup>[14]</sup> Ammonia is readily available from the Haber process.

Another route of hydrazine synthesis involves oxidation of urea with sodium hypochlorite:<sup>[15]</sup>

 $(H_2N)_2C=O + NaOCl + 2 NaOH \rightarrow N_2H_4 + H_2O + NaCl + Na_2CO_3$ 

Hydrazine can be synthesized from ammonia and hydrogen peroxide in the Pechiney-Ugine-Kuhlmann process, according to the following formula:

 $2\mathrm{NH}_3 + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{H}_2\mathrm{N}\text{-}\mathrm{NH}_2 + 2\mathrm{H}_2\mathrm{O}^{[16]}$ 

In the Atofina–PCUK cycle, hydrazine is produced in several steps from acetone, ammonia, and hydrogen peroxide. Acetone and ammonia first react to give the imine followed by oxidation with hydrogen peroxide to the oxaziridine, a three-membered ring containing carbon, oxygen, and nitrogen, followed by ammonolysis to the hydrazone, a process that couples two nitrogen atoms. This hydrazone reacts with one more equivalent of acetone, and the resulting acetone azine is hydrolyzed to give hydrazine, regenerating acetone. Unlike the Raschig process, this process does not produce salt. The PCUK stands for Produits Chimiques Ugine Kuhlmann, a French chemical manufacturer.<sup>[17]</sup>

Hydrazine can also be produced via the so-called ketazine and peroxide processes.

It was recently discovered that hydrazine is produced by some yeasts and the open ocean bacterium anammox (Brocadia anammoxidans). They are the only discovered organisms to naturally produce hydrazine.<sup>[18]</sup>

# Hydrazine derivatives

Many substituted hydrazines are known, and several occur naturally. Some examples include

- monomethyl hydrazine, where one of the hydrogen atoms on the hydrazine molecule has been replaced with a methyl group (CH<sub>3</sub>). By the symmetry of the hydrazine molecule, it does not matter which hydrogen atom is replaced. It is sometimes used as a rocket fuel.
- 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) and 1,2-dimethylhydrazine (symmetrical dimethylhydrazine) are hydrazines where two hydrogen atoms are replaced by methyl groups. UDMH is easier to manufacture than symmetrical dimethylhydrazine is, and UDMH is a fairly-common rocket fuel.
- gyromitrin and agaritine are hydrazine derivatives found in the commercially produced mushroom species *Agaricus bisporus*. Gyromitrin is metabolized into monomethyl hydrazine.
- Isoniazid, iproniazid, hydralazine, and phenelzine are medications whose molecules contain hydrazine-like structures.
- 2,4-dinitrophenylhydrazine (2,4-DNPH) is commonly used to test for ketones and aldehydes in organic chemistry.
- phenylhydrazine,  $C_6H_5$ NHNH<sub>2</sub>, the first hydrazine to be discovered.

# Applications

The majority use of hydrazine is as a precursor to blowing agents. Specific compounds include azodicarbonamide and azobis (isobutyronitrile), which yield 100-200 mL of gas per gram of precursor. In a somewhat related application, sodium azide, the gas-forming agent in air bags, is produced from hydrazine by reaction with sodium nitrite.<sup>[8]</sup> Hydrazine is also used as a propellant onboard space vehicles, and to both reduce the concentration of dissolved oxygen in and control pH of water used in large industrial boilers. Recently, hydrazine has been used to dissolve materials for solar cell applications by researchers at IBM and UCLA.<sup>[19]</sup> <sup>[20]</sup>

# **Organic chemistry**

Hydrazines are part of many organic syntheses, often those of practical significance in pharmaceuticals, such as the antituberculosis medication Isoniazid and the antifungal Fluconazole, as well as in textile dyes and in photography.<sup>[8]</sup>

### Hydrazone formation

Illustrative of the condensation of hydrazine with a simple carbonyl is its reaction with propanone to give the diisopropylidene hydrazine (acetone azine). The latter reacts further with hydrazine to afford the hydrazone:<sup>[21]</sup>

$$2 (CH_3)_2CO + N_2H_4 \rightarrow 2 H_2O + [(CH_3)_2C=N]_2$$
$$[(CH_3)_2C=N]_2 + N_2H_4 \rightarrow 2 (CH_3)_2C=NNH_2$$

The propanone azine is an intermediate in the Atofina-PCUK synthesis. Direct alkylation of hydrazines with alkyl halides in the presence of base affords alkyl-substituted hydrazines, but the reaction is typically inefficient due to poor control on level of substitution (same as in ordinary amines). The reduction of hydrazones to hydrazines present a clean way to produce 1,1-dialkylated hydrazines.

In a related reaction, 2-cyanopyridines react with hydrazine to form amide hydrazides, which can be converted using 1,2-diketones into triazines.

#### **Wolff-Kishner reduction**

Hydrazine is used in the Wolff-Kishner reduction, a reaction that transforms the carbonyl group of a ketone or aldehyde into a methylene (or methyl) group via a hydrazone intermediate. The production of the highly-stable dinitrogen from the hydrazine derivative helps to drive the reaction.

#### Heterocyclic chemistry

Being bifunctional, with two amines, hydrazine is a key building block for the preparation of many heterocyclic compounds via condensation with a range of difunctional electrophiles. With 2,4-pentanedione, it condenses to give the 3,5-dimethylpyrazole.<sup>[22]</sup> In the Einhorn-Brunner reaction hydrazines react with imides to give triazoles.

## Sulfonation

Being a good nucleophile,  $N_2H_4$  can attack sulfonyl halides and acyl halides.<sup>[23]</sup> The tosylhydrazine also forms hydrazones upon treatment with carbonyls.

### **Deprotection of phthalimides**

Hydrazine is used to cleave *N*-alkylated phthalimide derivatives. This scission reaction allows phthalimide anion to be used as amine precursor in the Gabriel synthesis.<sup>[24]</sup>

# **Reducing agent**

Hydrazine is a convenient reductant because the by-products are typically nitrogen gas and water. Thus, it is used as an antioxidant, an oxygen scavenger, and a corrosion inhibitor in water boilers and heating systems. It is also used to reduce metal salts and oxides to the pure metals in electroless nickel plating and plutonium extraction from nuclear reactor waste.

#### Hydrazinium salts

Hydrazine is converted to solid salts by treatment with mineral acids. A common salt is hydrazine sulfate,  $[N_2H_5]HSO_4$ , called hydrazinium sulfate.<sup>[25]</sup> Hydrazine sulfate was investigated as a treatment of cancer-induced cachexia, but proved ineffective.<sup>[26]</sup>

Hydrazine azide  $(N_5H_5)$ , the salt of hydrazine and hydrazoic acid, was of scientific interest, because of its high nitrogen content and explosive properties. Structurally, it is  $[N_2H_5]^+[N_3]^-$ . It decomposes explosively into hydrazine, ammonia and nitrogen gas:<sup>[27]</sup>

$$12 \text{ N}_5\text{H}_5 \rightarrow 3 \text{ N}_2\text{H}_4 + 16 \text{ NH}_3 + 19 \text{ N}_2$$

Reaction of  $N_5H_5$  with sulfuric acid gives quantitative yields of pure hydrazine sulfate and hydrazoic acid.<sup>[28]</sup>

# Other industrial uses

Hydrazine is used in many processes including: production of spandex fibers, as a polymerization catalyst; in fuel cells, solder fluxes; and photographic developers, as a chain extender in urethane polymerizations, and heat stabilizers. In addition, a semiconductor deposition technique using hydrazine has recently been demonstrated, with possible application to the manufacture of thin-film transistors used in liquid crystal displays. Hydrazine in a 70% hydrazine, 30% water solution is used to power the EPU (emergency power unit) on the Lockheed F-16 Fighting Falcon fighter plane. The explosive Astrolite is made by combining hydrazine with ammonium nitrate.

Hydrazine is often used as an oxygen scavenger and corrosion inhibitor in boiler water treatment. However due to the toxicity and certain undesired effects, namely increased rates of flow-accelerated corrosion (FAC), this practice is discouraged.

#### **Rocket fuel**

Hydrazine was first used as a rocket fuel during World War II for the Messerschmitt Me 163B (the first rocket-powered fighter plane), under the code name B-Stoff (hydrazine hydrate). When mixed with methanol (M-Stoff) and water it was called C-Stoff.

Hydrazine is also used as a low-power monopropellant for the maneuvering thrusters of spacecraft, and the Space Shuttle's auxiliary power units (APUs). In addition, monopropellant hydrazine-fueled rocket engines are often used in terminal descent of spacecraft. A collection of such engines was used in both Viking program landers as well as the Phoenix lander launched in August 2007.

In all hydrazine monopropellant engines, the hydrazine is passed by a catalyst such as iridium metal supported by high-surface-area alumina (aluminium oxide) or carbon nanofibers,<sup>[29]</sup> or more recently molybdenum nitride on alumina,<sup>[30]</sup> which causes it to decompose into ammonia, nitrogen gas, and hydrogen gas according to the following reactions:

- 1.  $3 \text{ N}_2\text{H}_4 \rightarrow 4 \text{ NH}_3 + \text{N}_2$ 2.  $N_2H_4 \rightarrow N_2 + 2H_2$ 3.  $4 NH_3 + N_2H_4 \rightarrow 3N_2 + 8H_2$

These reactions are extremely exothermic (the catalyst chamber can reach 800 °C in a matter of milliseconds,<sup>[29]</sup>) and they produce large volumes of hot gas from a small volume of liquid hydrazine,<sup>[30]</sup> making it a fairly efficient thruster propellant with a vacuum specific impulse of about 220 seconds.<sup>[31]</sup>

Hydrazine is also used in F-16 aircraft to power the EPU (emergency power unit). It is a small generator that supplies emergency hydraulic or electric power in the event that main power is lost in the aircraft.

Other variants of hydrazine that are used as rocket fuel are monomethylhydrazine, (CH2)NH(NH2) (also known as MMH) and unsymmetrical dimethylhydrazine, (CH<sub>3</sub>)<sub>2</sub>N(NH<sub>2</sub>) (also known as UDMH). These derivatives are used in two-component rocket fuels, often together with nitrogen tetroxide,  $N_2O_4$ , sometimes known as dinitrogen tetroxide. This reaction is extremely exothermic, as a rocket fuel must be, and the burning is also hypergolic, which means that the burning starts without any external ignition source.

## **Fuel cells**

The Italian catalyst manufacturer Acta has proposed using hydrazine as an alternative to hydrogen in fuel cells. The chief benefit of using hydrazine is that it can produce over 200 mW/cm<sup>2</sup> more than a similar hydrogen cell without the need to use expensive platinum catalysts. As the fuel is liquid at room temperature, it can be handled and stored more easily than hydrogen. By storing the hydrazine in a tank full of a double-bonded carbon-oxygen carbonyl, the fuel reacts and forms a safe solid called hydrazone. By then flushing the tank with warm water, the liquid hydrazine hydrate is released. Hydrazine has a higher electromotive force of 1.56 V compared to 1.23 V for hydrogen. Hydrazine breaks down in the cell to form nitrogen and hydrogen which bonds with oxygen, releasing water.<sup>[32]</sup> Hydrazine was used in fuel cells manufactured by Allis-Chalmers Corp., including some that provided electric power in space satellites in the 1960s.

# Safety

Hydrazine is highly toxic and dangerously unstable, especially in the anhydrous form. According to the U.S. **Environmental Protection Agency:** 

Symptoms of acute (short-term) exposure to high levels of hydrazine may include irritation of the eyes, nose, and throat, dizziness, headache, nausea, pulmonary edema, seizures, coma in humans. Acute exposure can also damage the liver, kidneys, and central nervous system. The liquid is corrosive and may produce dermatitis from skin contact in humans and animals. Effects to the lungs, liver, spleen, and thyroid have been reported in animals chronically exposed to hydrazine via inhalation. Increased incidences of lung, nasal cavity, and liver tumors have been observed in rodents exposed to hydrazine.<sup>[33]</sup>

Limit tests for hydrazine in pharmaceuticals suggest that it should be in the low ppm range.<sup>[34]</sup> Hydrazine may also cause steatosis.<sup>[35]</sup> At least one human is known to have died, after 6 months of sublethal exposure to hydrazine hydrate.<sup>[36]</sup>

On February 21, 2008, the United States government destroyed the disabled spy satellite USA 193 with a sea-launched missile, reportedly due to the potential danger of a hydrazine release if it re-entered the Earth's atmosphere intact.<sup>[37]</sup>

# See also

- Hydrazine sulfate
- List of Stoffs
- USA 193

# **External links**

- The Late Show with Rob! Tonight's Special Guest: Hydrazine (PDF)<sup>[38]</sup> Robert Matunas
- Hydrazine chemical product info: properties, production, applications. <sup>[39]</sup>
- Hydrazine toxicity <sup>[40]</sup>

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