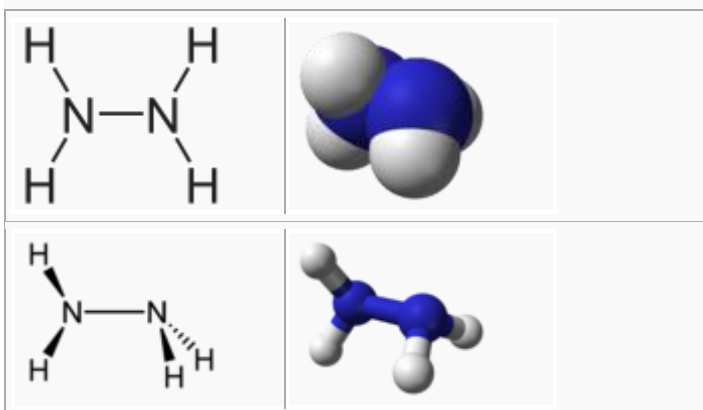


Hydrazine

Hydrazine is an inorganic compound with the chemical formula H_2NNH_2 (also written N_2H_4). It is a colorless flammable liquid with an ammonia-like odor. Hydrazine is highly toxic and dangerously unstable unless handled in solution. As of 2000, approximately 120,000 tons of hydrazine hydrate (corresponding to a 64% solution of hydrazine in water by weight) were manufactured worldwide per year. 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. Hydrazine is used within both nuclear and conventional electrical power plant steam cycles as an oxygen scavenger to control concentrations of dissolved oxygen in an effort to reduce corrosion.

Hydrazine



Molecular structure

Each $\text{H}_2\text{N-N}$ subunit is pyramidal in shape. The N-N single bond distance is 1.45 Å (145 pm), and the molecule adopts a gauche conformation. The rotational barrier is twice that of ethane. These structural properties resemble those of gaseous hydrogen peroxide, which adopts a "skewed" anticline conformation, and also experiences a strong rotational barrier.

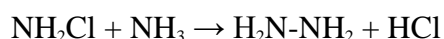
Synthesis and production

Different routes have been developed over the years: the key step is the creation of the nitrogen-nitrogen single bond. In the Olin Raschig process, chlorine-based oxidants oxidize ammonia without the presence of ketone. In the peroxide process, hydrogen peroxide

oxidizes ammonia in the presence of ketone. Instead of carbon-nitrogen double bond in imine, urea provides amine groups bonded to carbonyl for oxidation.

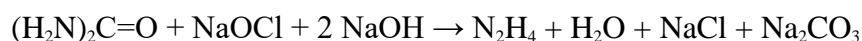
Oxidation by chloramine from hypochlorite on ammonia

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 to create the nitrogen-nitrogen single bond as well as a hydrogen chloride byproduct:



Oxidation of urea by hypochlorite

Related to the Raschig process, urea can be oxidized instead of ammonia. Again sodium hypochlorite serves as the oxidant. The net reaction is shown:



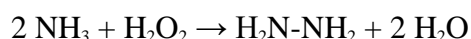
The process generates significant byproducts and is mainly practiced in Asia.

Oxidation by chloramine from hypochlorite on ammonia in presence of acetone

The Bayer Ketazine Process is the predecessor to the peroxide process. It employs sodium hypochlorite as oxidant instead of hydrogen peroxide. Like all hypochlorite-based routes, this method suffers from the fact that it produces an equivalent of salt for each equivalent of hydrazine.

Oxidation by oxaziridine from peroxide on ammonia

Hydrazine can be synthesized from ammonia and hydrogen peroxide in the peroxide process (sometimes called Pechiney-Ugine-Kuhlmann process, the Atofina-PCUK cycle, or ketazine process). The net reaction follows:



In this route, hydrazine is produced in several steps from ammonia, hydrogen peroxide, and a ketone such as acetone or methylethyl ketone. The ketone and ammonia first condense to give the imine, which is oxidised by hydrogen peroxide to the oxaziridine, a three-membered ring containing carbon, oxygen, and nitrogen. Next, the oxaziridine gives

the hydrazone by treatment with ammonia, a process creating the nitrogen-nitrogen single bond. This hydrazone condenses with one more equivalent of ketone; the resultingazine is hydrolyzed to give hydrazine and regenerate the ketone. Unlike the Olin Raschig Process, this approach does not produce a salt as a by-product.

Applications

Main uses

The majority use of hydrazine is as a precursor to blowing agents. Specific compounds include azodicarbonamide and azobisisobutyronitrile, which yield 100-200 mL of gas per gram of precursor. In a related application, sodium azide, the gas-forming agent in air bags, is produced from hydrazine by reaction with sodium nitrite.

Hydrazine is also used as a propellant on board space vehicles, and to both reduce the concentration of dissolved oxygen in and control pH of water used in large industrial boilers. The F-16 fighter jet uses hydrazine to fuel the aircraft's emergency power unit.

Precursor to pesticides and pharmaceuticals

Hydrazine is a precursor to several pharmaceuticals and pesticides. Often these applications involve conversion of hydrazine to the heterocycles pyrazoles and pyridazines. Examples of commercialized bio-active hydrazine derivatives include 3-amino-1,2,4-triazole, Cefazolin, Rizatriptan, Anastrozole, Fluconazole, Metazachlor, Pyridazine, Metamitron, Pyrazole, Metribuzin, Paclobutrazol, Diclobutrazole, Propiconazole, and Triadimefon.

Small-scale, niche, and historic uses

Rocket fuel

Anhydrous hydrazine being loaded into the *MESSENGER* space probe. The technician is wearing a safety suit.

Hydrazine was first used during World War II as a component of the rocket fuel, in a 30% mix by weight with both a 57% methanol content (itself called M-Stoff) and 13% water, it was called C-Stoff, for the Messerschmitt Me 163B (the first rocket-powered fighter plane), and hypergolic with the high test peroxide based *T-Stoff* oxidizer. Hydrazine used alone by the

World War II Germans received the alternative name of **B-Stoff**, a designation also used later for the *Brennstoff* methanol/water fuel for the V-2 missile.

Hydrazine is used as a low-power monopropellant for the maneuvering thrusters of spacecraft, and was used to power the Space Shuttle's auxiliary power units (APUs). In addition, monopropellant hydrazine-fueled rocket engines are often used in terminal descent of spacecraft. Such engines were used on the Viking program landers in the 1970s as well as the Phoenix lander and Curiosity rover which landed on Mars in May 2008 and August 2012, respectively.

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, or more recently molybdenum nitride on alumina, 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. $\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$
3. $4\text{NH}_3 + \text{N}_2\text{H}_4 \rightarrow 3\text{N}_2 + 8\text{H}_2$

Reactions 1 and 2 are extremely exothermic (the catalyst chamber can reach 800 °C in a matter of milliseconds,) and they produce large volumes of hot gas from a small volume of liquid, making hydrazine a fairly efficient thruster propellant with a vacuum specific impulse of about 220 seconds. Reaction 3 is endothermic and so reduces the temperature of the products, but also produces a greater number of molecules. The catalyst structure affects the proportion of the NH_3 that is dissociated in Reaction 3; a higher temperature is desirable for rocket thrusters, while more molecules are desirable when the reactions are intended to produce greater quantities of gas

Other variants of hydrazine that are used as rocket fuel are monomethylhydrazine, $(\text{CH}_3)\text{NH}(\text{NH}_2)$ (also known as MMH), and unsymmetrical dimethylhydrazine, $(\text{CH}_3)_2\text{N}(\text{NH}_2)$ (also known as UDMH). These derivatives are used in two-component rocket fuels, often together with dinitrogen tetroxide, N_2O_4 . These reactions are extremely exothermic, and the burning is also hypergolic, which means that it starts without any external ignition source.

There are ongoing efforts to replace hydrazine along with other highly toxic substances from the aerospace industry. Promising alternatives include hydroxylammonium nitrate, 2-Dimethylaminoethylazide (DMAZ) and energetic ionic liquids.

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/cm² 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. Hydrazine was used in fuel cells manufactured by Allis-Chalmers Corp., including some that provided electric power in space satellites in the 1960s.

Gun propellant

A mixture of 63% hydrazine, 32% hydrazine nitrate and 5% water is a standard propellant for experimental bulk-loaded liquid propellant artillery. The propellant mixture above is one of the most predictable and stable, with a flat pressure profile during firing. Misfires are usually caused by inadequate ignition. The movement of the shell after a misignition causes a large bubble with a larger ignition surface area, and the greater rate of gas production causes very high pressure, sometimes including catastrophic tube failures (i.e. explosions)