

Compounds of s- and p-Block Elements

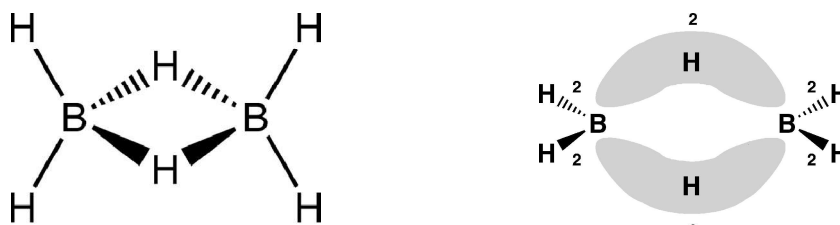
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Topics

Diborane and concept of multicentre bonding

Hydrides of nitrogen (NH_3 , N_2H_4 , N_3H , NH_2OH)

Diborane

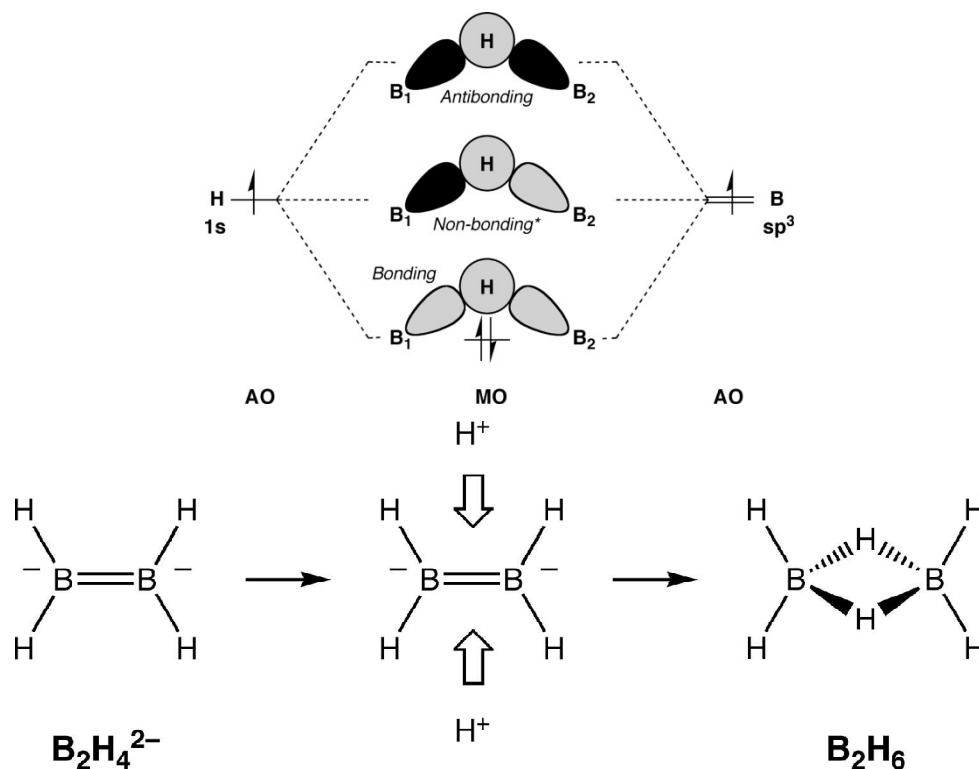


Is Diborane electron deficient compound?

If we consider the molecule B_2H_6

there are 12 valence electrons (**B has 3, and H has 1, so $2 \times \text{B} + 6 \times \text{H} = 12$**).

Each terminal B–H bond is a standard called *two centered two electron bond* (i.e., **3C-2e** bond), and there are four of these, thus accounting for a total of eight electrons. This leaves a total of four electrons to share between the two bridging H atoms and the two B atoms. Consequently, two B–H–B bridging bonds are formed, Each of which consists of two electrons, forming what are called *three center-two-electron bonds* (i.e., **3C-2e** bond)) sometimes called ‘banana’ bonds, as they are not linear but curved.



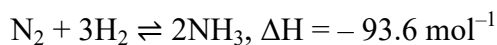
Each B atom is, approximately, sp^3 hybridized hybridization is just a mathematical tool, so you can just as easily have $s^{1.05} p^{2.95}$ hybridized orbitals!), and if we consider just one of the B atoms, two of the four sp^3 hybrid orbitals form σ bonds to the terminal H atoms ($1s$ orbitals). That leaves two B sp^3 hybrid orbitals, one of which contains an electron, one of which is empty. For each bridge therefore, one sp^3 orbital from each of the B atoms combines (**Figure 3**) with the $1s$ orbital of the bridging H atom to form three new molecular orbitals (MOs) – as always, n atomic orbitals (AO) form n MOs. One B atom gives its remaining valence electron to one bridge, and the other B atom gives to the other. Each bridge, therefore, has two electrons, which fill our new MO scheme starting with the lowest energy bonding MO.

Hydrides of nitrogen

Ammonia

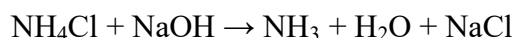
Ammonia is the most important compound of nitrogen. It can be manufactured by Haber's process.

In this process, a mixture of N_2 and H_2 in the ratio of 1 : 3 is passed over heated Fe at 650–800 K as catalyst and Mo as promotor,



This is a reversible exothermic reaction.

Ammonia is prepared in the laboratory by heating ammonium salt (NH_4Cl) with a strong alkali like NaOH



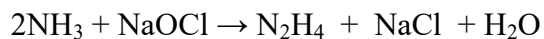
Ammonia can be dried by passing over quick lime (CaO). However, it cannot be dried with dehydrating agents such as conc. H_2SO_4 , P_2O_5 and anhydrous CaCl_2 because ammonia reacts with these compounds.

NH_3 is a colourless gas with a characteristic pungent smell called ammoniacal smell. It is highly soluble in water and its solution is basic in nature, $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. NH_3 is expected to have a tetrahedral geometry, but the lone pair distorts its geometry and the molecule has pyramidal geometry with N – H bond length of 101.7 pm and a bond angle of 107.5° . Liquid ammonia is widely used as a refrigerant due to its high heat of vaporization

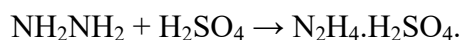
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Hydrazine, ($\text{NH}_2 - \text{NH}_2$)

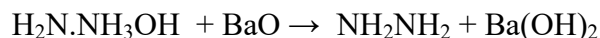
Hydrazine is prepared commercially by boiling aqueous ammonia or urea with sodium hypochloride in the presence of glue or gelatin.



The resulting solution is concentrated and anhydrous hydrazine may be obtained by further distillation over barium oxide. Alternatively, the hydrazine present in the resulting solution is precipitated as sparingly soluble crystalline hydrazine sulphate on treatment with sulphuric acid,



The precipitate is removed and treated with an alkali when hydrazine hydroxide $\text{H}_2\text{N.NH}_3\text{OH}$ is obtained. This is distilled under reduced pressure, over barium oxide to liberate free hydrazine.



Physical properties : Anhydrous hydrazine is a colourless fuming liquid (m.p. 2°C and b.p. 114°C) soluble in water in all proportions. It is also soluble in alcohol. It is strongly hygroscopic.

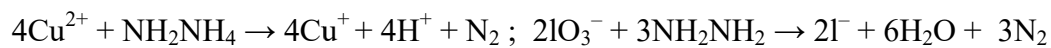
Chemical properties : It behaves as a diacid base, Thus with hydrochlorides it forms hydrazine monochloride $\text{H}_2\text{N.NH}_3\text{Cl}$ and hydrazine dichloride $\text{ClH}_3\text{N.NH}_3\text{Cl}$.

(i) Hydrazine burns in air with the evolution of heat.



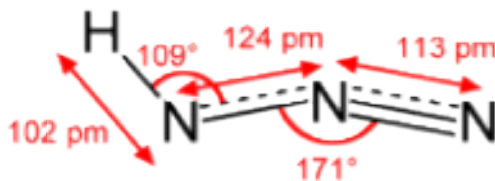
The alkyl derivative of hydrazine are used as rocket fuels.

(ii) It reduces Fehling's solution to red cuprous oxide and iodates to iodides.



Uses : Hydrazine is used as a rocket fuel. It is also used as a reagent in organic chemistry.

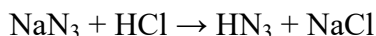
Hydrazoic Acid ($\text{N}_3 \text{H}$)



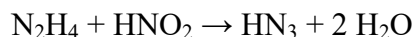
Hydrazoic acid, also known as hydrogen azide or azoimide, is a compound with the chemical formula HN_3 . It is a colorless, volatile, and explosive liquid at room temperature and pressure. It is a compound of nitrogen and hydrogen, and is therefore a pnictogen hydride. It was first isolated in 1890 by Theodor Curtius.

Synthesis of Hydrazoic Acid

Hydrazoic acid is usually formed by acidification of an azide salt like sodium azide.

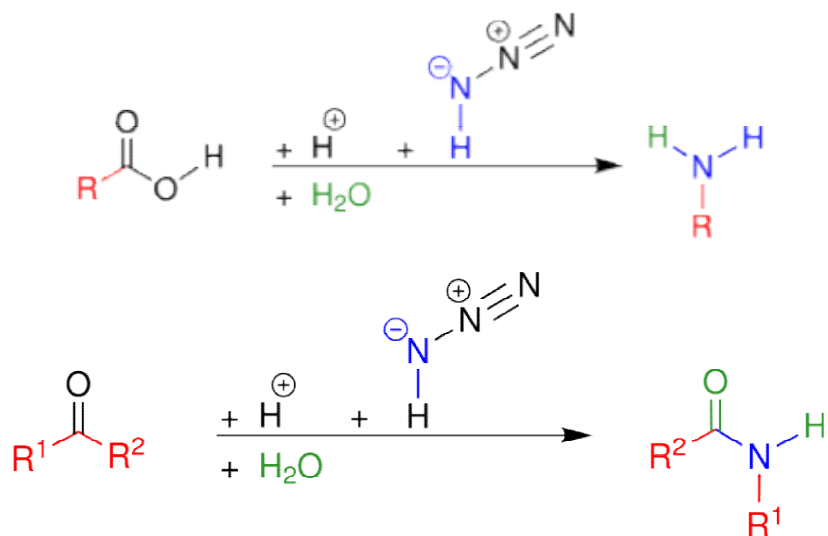


It was originally prepared by the reaction of aqueous hydrazine with nitrous acid.



Physical properties: The pure acid is an extremely explosive colorless liquid with an unpleasant smell.

Chemical properties: Hydrazoic acid may react with carbonyl derivatives, including aldehydes, ketones, and carboxylic acids, to give an amine or amide, with expulsion of nitrogen. This is known as Schmidt reaction or Schmidt rearrangement.



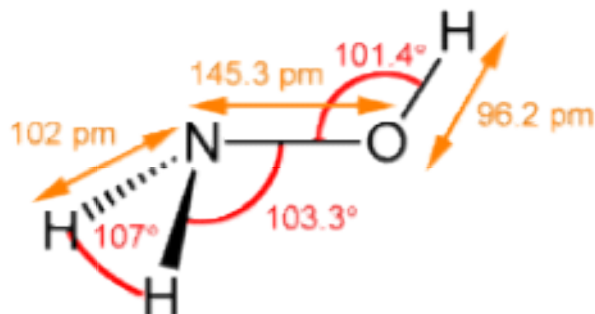
Uses of Hydrazoic Acid

2-Furonitrile, a pharmaceutical intermediate and potential artificial sweetening agent has been prepared in good yield by treating furfural with a mixture of hydrazoic acid (HN₃) and perchloric acid in the presence of magnesium perchlorate in the benzene solution at 35 °C.

The all gas-phase iodine laser (AGIL) mixes gaseous hydrazoic acid with chlorine to produce excited nitrogen chloride, which is then used to cause iodine to lase; this avoids the liquid chemistry requirements of COIL lasers.

Hydroxylamine (NH₂ OH)

Hydroxylamine was first prepared as hydroxylamine hydrochloride in 1865 by the German chemist Wilhelm Clemens Lossen. It was first prepared in pure form in 1891 by the Dutch chemist Lobry de Bruyn and by the French chemist Léon Maurice Crismer.

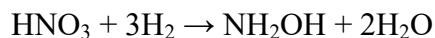


Synthesis of Hydroxylamine

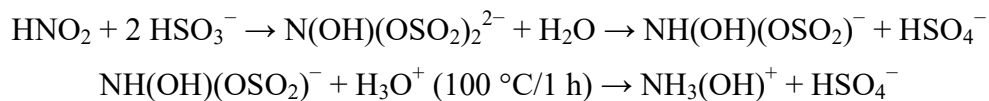
NH₂OH can be produced via several routes. The main route is via the Raschig process: aqueous ammonium nitrite is reduced by HSO₃⁻ and SO₂ at 0 °C to yield a hydroxylamido-N,N-disulfonate anion.



Julius Tafel discovered that hydroxylamine hydrochloride or sulfate salts can be produced by electrolytic reduction of nitric acid with HCl or H₂SO₄ respectively



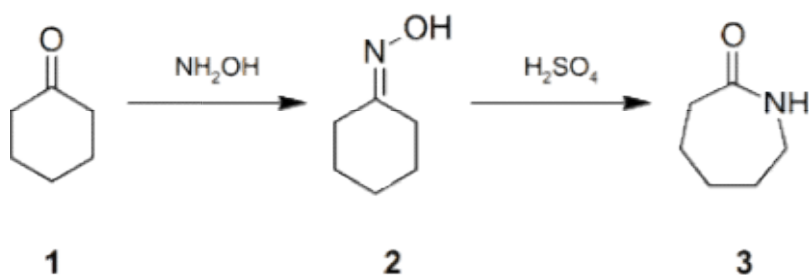
Hydroxylamine can also be produced by the reduction of nitrous acid or potassium nitrite with bisulfite:



Uses of Hydroxylamine

Hydroxylamine and its salts are commonly used as reducing agents in various organic and inorganic reactions:

Backmann rearrangement: Conversion of Cyclohexanone to Caprolactam



Hydroxylamine can also be used to highly selectively cleave asparaginy-glycine peptide bonds in peptides and proteins. It also bonds to and permanently disables (poisons) heme-containing enzymes. It is used as an irreversible inhibitor of the oxygen-evolving complex of photosynthesis on account of its similar structure to water.

An alternative industrial synthesis of paracetamol developed by Hoechst–Celanese involves the conversion of ketone to a ketoxime with hydroxylamine.

References:

1. *Concise Inorganic Chemistry*: J. D. Lee
2. *Basic Inorganic Chemistry*: F.A. Cotton & G. Wilkinson
3. *Inorganic Chemistry*: D. F. Shriver and P. W. Atkins
4. *Wikipedia*