COMPOUNDS OF NITROGEN

Nitrogen forms more than 20 binary compounds with hydrogen of which ammonia, hydrazine and hydrogen azide are most important. Though many salts of ammonium is known, ammonium hydride [NH_5] is unknown. N_2H_2 is diazene, N_3H_3 is triazene etc.

HYDRAZINE [N_2H_4]

Fuming, colourless, hygroscopic liquid with faint ammoniacal odour. Soluble in alcohol and water. B Pt. 113.5°C

PREPARATIONS:

1. **RASCHIG'S METHOD:** Hydrazine can be prepared by the action of sodium hypochlorite upon ammonia in large excess, in presence of little *glue or gelatine.*

   $$NH_3 + NaOCl = NH_2Cl + NaOH \quad ; \quad NH_2Cl + NH_3 = N_2H_4 + HCl$$

Role of Glue/ Gelatine

The yield of hydrazine may be much reduced by the side reaction:

$$2NH_2Cl + N_2H_4 = N_2 + 2NH_4Cl$$

The above reaction is catalysed by the presence of the trace ferric or cupric ions. Such ions may be removed by the presence of glue/gelatine. Addition of a little EDTA is also effective.

2. ***Anhydrous hydrazine*** is more easily prepared by adding a solution of sodium methoxide in methyl alcohol to a solution of hydrazine hydrochloride in , methyl alcohol. Sodium chloride produced is filtered off and then distillation gives anhydrous hydrazine after methanol is distilled off.

   $$N_2H_4.HCl + CH_3ONa = N_2H_4 + CH_3OH + NaCl$$

Chemical Properties:

Decomposition: $3N_2H_4 = N_2 \uparrow + 4NH_3$

Oxidation: $N_2H_4 + O_2 = N_2 \uparrow + 2H_2O$

$3\,N_2H_4 + 5O_3 = 2N_3H + 5H_2O + 5O_2 \uparrow$

$3\,N_2H_4 + 5H_2O_2 = 2N_3H + 10H_2O$

Ozone and hydrogen peroxide oxidise it to Hydrazoic acid.

Basic properties: Hydrazine is a very weak base , much weaker than ammonia. Hydrazine usually functions as monoacidic base. $N_2H_4.H_2SO_4$ & $N_2H_4.HCl$ are well known ionic solids.

Hydrazine is a powerful reducing agent:

$N_2H_4 = N_2 \uparrow + 4H^+ + 4e$ **[in acid medium]**

$N_2H_4 + 4OH^- = N_2 \uparrow + 4H_2O + 4e$ **[in basic medium]**

$4CuO(black) + N_2H_4 = 2Cu_2O\ (Red)\downarrow + N_2 \uparrow + 2H_2O$

$4Fe^{3+} + N_2H_4 = 4Fe^{2+} + N_2 \uparrow + 4H^+$

$4KMnO_4 + 6H_2SO_4 + 5N_2H_4 = 2K_2SO_4 + 4MnSO_4 + 16H_2O + 5N_2 \uparrow$

$4AgNO_3 + N_2H_4 = 4Ag \downarrow + 4HNO_3 + N_2 \uparrow$

$PtCl_4 + N_2H_4 = Pt \downarrow + 4HCl + N_2\uparrow$

$N_2H_4 + 2X_2 = N_2 \uparrow + 4HX$ **[X = Cl, Br, I]**

$4K_3Fe(CN)_6 + 4KOH + N_2H_4 = 4K_4Fe(CN)_6 + N_2 \uparrow + 4H_2O$
$4AuCl_3 + 3\ N_2H_4 = 4Au \downarrow + 12HCl + N_2 \uparrow$

Hydrazine can act as oxidant: $N_2H_4 + 4H^+ + 2Ti^{3+} = 2NH_4^+ + 2Ti^{4+}$

USE: Hydrazine is used as rocket fuel, anti T.B drug, and also as reducing agent in analytical chemistry. On February 21, 2008, the United States government destroyed the disabled spy satellite USA 193 with a sea-launched missile, purportedly due to the potential danger of a hydrazine release if it re-entered the Earth's atmosphere intact.

STRUCTURE: Hydrazine have unsymmetrical structure with both nitrogens are sp^3 (Dipole moment = 1.85 D). Hydrazine can arise via coupling a pair of ammonia molecules by removal of one hydrogen per molecule. Each H_2N-N subunit is pyramidal in shape. The N-N 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" anticlinal conformation, and also experiences a strong rotational barrier.

HYDRAZOIC ACID [HN_3]: Hydrogen azide is a colourless highly poisonous, dangerously explosive liquid with an offensive smell. Soluble in water, in which it is 1% ionised. It is as strong as acetic acid (pKa =4.77)

PREPARATIONS:

1. Aqueous solutions of HN_3 were first prepared in 1890 by T. Curtius who oxidised aqueous hydrazine with nitrous acid.

$$N_2H_5^+ + HNO_2 = HN_3 + H^+ + 2H_2O$$

Other oxidising agents that can be used include nitric acid, hydrogen peroxide, peroxydisulfate, chlorate etc.

2. (i) When sodium metal heated to about 200°C and a current of dry ammonia is passed over it, sodamide, $NaNH_2$ is obtained. $2Na + 2NH_3 = 2NaNH_2 + H_2 \uparrow$
   (ii) When no more hydrogen gas is evolved , in the same test tube nitrous oxide is passed. Sodium azide thus obtained then distilled with dil. H_2SO_4 to prepare hydrazoic acid.
   $NaNH_2 + N_2O = NaN_3 + H_2O$
   $2NaN_3 + H_2SO_4 = Na_2SO_4 + 2HN_3$

Chemical Properties:

Decomposition: it is decomposed by HCl, HI etc. giving dinitrogen.
$HN_3 + 2HI = NH_3 + N_2 \uparrow + I_2 \uparrow$

$2HN_3 = 3N_2 \uparrow + H_2 \uparrow + 123.3$ **Kcal**

Reduction :

It is reduced to ammonia or hydrazine by sodium amulgum or finely divided Pt

$$HN_3 + 4H_2 = 3NH_3$$
$$2\,HN_3 + 5H_2 = 3N_2H_4$$
$$Sn^{2+} + 3H^+ + HN_3 = Sn^{4+} + NH_4^+ + N_2$$

Oxidation: $HN_3 + HNO_2 = N_2 + N_2O + H_2O$

$2HN_3 + HOCl = 3N_2\uparrow + HCl + H_2O$

$2HN_3 + O(\text{from } KMnO_4) = 3N_2\uparrow + H_2O$

STRUCTURE: HN_3 molecule has a bent structure with linear N-N-N skeleton. X-ray diffraction of ionic azides shows both N-N lengths are equal(1.16Å)

HYDROXYLAMINE, NH_2OH

Pure hydroxylamine is poisonous, colourless, odourless thermally unstable hygroscopic compound which is usually handled in aqueous solution or in the form of one of its salts.
Soluble in water and alcohol, but only slightly in ether or benzene.

Basic Property: Hydroxylamine is a weaker base than ammonia and its aqueous solution precipitates hydroxides of many metals e.g., Zn & Al.

PREPARATIONS:

1. *Reduction of nitric oxide:* When nitric oxide is passed through a mixture of granulated tin and concentrated hydrochloric acid(containing a few drops of platinic acid so that platinum deposits on tin and form a galvanic couple) hydroxylamine hydrochloride is formed. A little of ammonium chloride is also formed.
   $NO + 3H + HCl = NH_2OH.HCl$
2. *Electrolytic reduction of nitric acid:* The electrolysis is carried out in a divided cell with lead electrodes using 50% sulphuric acid as electrolyte & 50% nitric acid is added dropwise in cathodic compartment. Cathodic reduction of nitric acid gives hydroxylamine.
   $HNO_3 + 6H = NH_2OH + 2H_2O$

3. *Reduction of sodium nitrite:* Hydroxylamine is formed by reduction of sodium nitrite solution by sulphur dioxide in presence of sodium carbonate (sodium nitrite : sodium carbonate in 2:1 molar ratio) at low temperature (-2°C) preferably buffered to pH = 4.3.
   $NaNO_2 + NaHSO_3 + SO_2 + 2H_2O = 2NaHSO_4 + NH_2OH$
4. *Anhydrous hydroxylamine:* Anhydrous hydroxylamine can be prepared by treating a suspension of hydroxylammonium chloride in butanol with sodium butoxide.
   $[NH_3OH]Cl + NaOBu = NH_2OH + NaCl + BuOH$

CHEMICAL PROPERTIES:

Decomposition: decomposes by disproportionation
$3NH_2OH = N_2 + NH_3 + 3H_2O$
$4NH_2OH = N_2O + 2NH_3 + 3H_2O$

Reducing property: Hydroxylamine hydrochloride is a powerful reducing agent.

In Acid Medium:
$4Fe^{3+} + 2NH_2OH = 4Fe^{2+} + N_2O + 4H^+ + H_2O$

In Alkaline Medium:
$4CuO + 2NH_2OH = 2Cu_2O + N_2O + 3H_2O$
$2I_2 + 2NH_2OH = 4HI + N_2O + H_2O$

Oxidising property:

In Alkaline Medium:
$NH_2OH + H_2O_2 = O_2 + NH_3 + H_2O$
$NH_2OH + 2Fe(OH)_2 + H_2O = 2Fe(OH)_3 + NH_3$
$NH_2OH + Na_3AsO_3 = Na_3AsO_4 + NH_3$

In Acid Medium:
$NH_2OH + 3H^+ + 2I^- = NH_4^+ + I_2 + H_2O$

HYDROXYLAMINE REACTS WITH ALDEHYDES AND KETONES TO GIVE OXIMES[C=N-OH]

USE: Used as reagent in analytical & organic chemistry. Also used to prepare caprolactum , a key intermediate in the production of polyamide-6 fibres such as nylon. World production is 650 000 tons/year.

STRUCTURE: NH_2OH can exist in *cis*- or *trans*- isomer. Central nitrogen is sp^3. The N-O distance is 147 pm