19.03.2020

Gp - 13 → Diborane :→ detailed discussion already done in class

Inert pair effect of group 13. discussed in class. and its diagonal relationship also discussed in class-

GROUP 15 :-

Elements of Group 15.

N, P, As, Sb, Bi.
→ down the group.

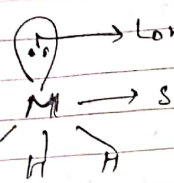
→ Hydrides of Nitrogen to be discussed.

NH_3, N_2H_4, N_3H, NH_2OH.
↓ Ammonia ↓ Hydrazine ↓ Hydrazoic acid ↓ Hydroxylamine

Hydrides of gp. 15

NH_3 : PH_3 AsH_3 SbH_3 BiH_3
Ammonia ↓ Phosphine ↓ Arsine ↓ Stibine ↓ Bismuthine

General Structure of hydrides



3 σ bonds are formed b/w M–H and one lone pair of e⊖s. is present on the metal

sp^3 hybridization takes place

Some Important properties of hydrides of Gp 15

1) Ammonia is soluble in water due to H-bonding b/w NH_3 & H_2O

2) Among all gp 15 hydrides the boiling point of NH_3 is higher than PH_3 & AsH_3 due to intermolecular H-bonding. As we move down the group the vander-Waals forces of attraction increase and we observe the following order of bpt.

$NH_3 > PH_3 < AsH_3 < SbH_3$

3) Prepn of Hydrides.

(1) Prepn of Ammonia → Haber's process

$$N_2 + 3H_2 \xrightarrow[200\ atm]{700\ K} 2NH_3$$

Ratio 1 : 3

The reaction proceeds according to La Chatelieri principle. High pressure favours formation of NH_3. Catalyst such as Iron oxide with small amounts of K_2O & Al_2O_3 is used to aquire fast equilibrium rate.

(ii) Binary metal compds such as Ca_3P_2 / Mg_3N_2 by hydrolysis with H_2O -

a) $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

b) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

4) MPts of hydrides

$PH_3 < AsH_3 < SbH_3 < NH_3$

NH_3 has H-bonding (Intermolecular)

so it has highest melting point the Mpt increases down the group due to corresponding increase in vander Waals forces of attraction.

5. Basic strength of hydrides

$NH_3 > PH_3 > AsH_3 > SbH_3 > NH_3$

due to the presence of lone pair of $e^{\ominus}$s in all the hydrides all the hydrides act as Lewis bases.

NH_3 is the strongest lewis base as Nitrogen has highest $e^{\ominus}$ density due to its smallest size among the group.

6. Bond angles of Hydrides.

$NH_3 > PH_3 > AsH_3 > SbH_3$.

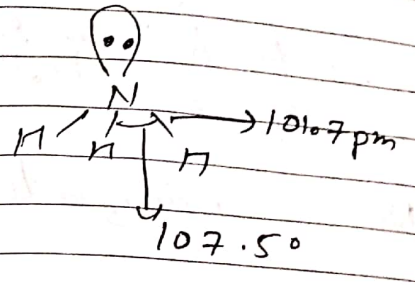
$107.8^\circ \quad 93.6^\circ \quad 91.8^\circ \quad 91.3^\circ$

Nitrogen has highest $e^{\ominus}$ density.

→ Higher the $e^{\ominus}$-vity of atom more will the $e^{\ominus}$s like closer to atom and more will be bond-pair bond-pair repulsions and greater would be the bond angle

↑Electronegativity ∝ Concentration of atom ∝ bp-bp repulsions

Structure of NH_3



Properties of NH_3

(i) NH_3 is Colourless gas, soluble in water, easily liquified by cooling under pressure

(ii) Liquified NH_3 is also known as as liquid ammonia. It boils at 239.7 K and freezes at 198.4K

(iii) NH_3 in water is known as aqueous solution of NH_3. It is weakly basic due to formation of OH^- ions.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

(iv) Ammonia can act as a reducing agent in following ways

$$2NH_3 + \overset{+2}{Cu}O \xrightarrow{\Delta} \overset{0}{Cu} + 3H_2O + N_2$$

Here Ammonia is oxidized to Nitrogen

thereby reducing $\overset{(+2)}{CuO}$ to $\overset{(0)}{Cu}$

→ Illy, in the following rxn.

$4NH_3 + SO_2 \xrightarrow{Pt,\ 1100K} 4NO + 6H_2O$

NH_3 is oxidized to NO

(V) NH_3 can donate its lone pair of e⁻s to form coordinate bond. as shown below in following cases

a) $NH_3 + BF_3 \rightarrow H_3N: \rightarrow BF_3$

here Ammonia BF_3 complex is formed

b) Copper ion dissolves in ammonia

$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$ (aq)

blue coloured.

c) White ppt of AgCl dissolves in excess of Ammonia to form coordination compound in following way.

$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$

Diammine silver (I) chloride

d) Illy $CuSO_4$ dissolves in NH_3 (excess) to form deep blue coloured complex

$CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + H_2O$.

7. Action of Halogens.

a) $8NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$
excess

b) $8NH_3 + 3Br_2 \rightarrow 6NH_4Br + N_2$

(c) $2NH_3 + 3I_2 \rightarrow NH_3.NI_3 + 3HI$

Nitrogen triiodide ammoniate

$8NH_3.NI_3 \xrightarrow{\text{Explode}} 5N_2 + 9I_2 + 6NH_4I$

↓

Harmless explosive.

8. One very important reaction of NH_3 is its reaction with CO_2 at 453 - 473 K, at 220 atm pressure. to form ammonium Carbamate which finally forms urea

$2NH_3 + CO_2 \xrightarrow[220\,atm]{453-473K} [NH_2COONH_4]$

$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$

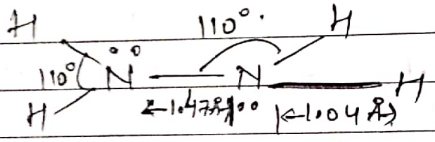
9. $2NH_3 + NaOCl \longrightarrow NH_2NH_2 + NaCl + H_2O$
Sodium hypochlorite. (Hydrazine)

Uses of Ammonia

a) Laboratory reagent
b) Cleaning agent for grease removal
c) Refrigerant.
d) Manufacture of fertilizers

HYDRAZINE

Structure



→ Unsymmetrical Structure.
→ Each N atom sp^3 hybridized

N–N distance = 1.47 Å.
N–H distance = 1.04 Å.

Properties of Hydrazine

1) Colourless liquid (fuming) Mpt = 113.5°C.

2) Hygroscopic, poisonous.

3) On heating N_2H_4 decomposes to give NH_3 and N_2

$3N_2H_4 \xrightarrow{\Delta} N_2 + 4NH_3$

4) N_2H_4 in presence of Zn & HCl is reduced to NH_3

$N_2H_4 + 2H \xrightarrow{Zn/HCl} 2NH_3$

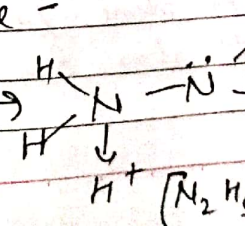
5) N_2H_4 on reaction with alkali metals forms, hydrazides. $M^+(N_2H_3)^-$ and H_2

$\Rightarrow N_2H_4 + Na \longrightarrow Na^+[N_2H_3]^- + \frac{1}{2}H_2$
Sodium hydrazide

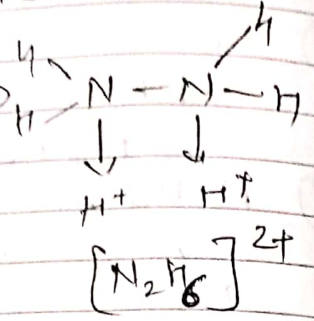
Imp

6) N_2H_4 is a diacidic base. N_2H_4 reacts with mineral acids like HCl, H_2SO_4 where one or both lone pair of e⊖s of N are donated to H^+ ion obtained by ionization of acid and hydrazinium ion ($N_2H_5^+$) or ($N_2H_6^{2+}$) (hydrazonium ion) are formed

$HCl \longrightarrow H^+ + Cl^-$

$N_2H_4 + H^+ \longrightarrow$ 

$2HCl \rightarrow 2H^+ + Cl^-$

$N_2H_4 + 2H^+ \rightarrow$ 

$[N_2H_6]^{2+}$

Uses of Hydrazine

1) Used as Rocket fuel and anti-TB drug.
2) Used as reducing agent

HYDRAZOIC ACID.

Structure

Unsymmetrical covalent molecule having bent structure where all the three N-atoms lie in the same line but H-atom lies out of line

PROPERTIES OF HYDRAZOIC ACID.

1) Colourless, highly volatile liquid mpt = $-80°C$ and bpt = $37°C$
2) Highly soluble in water, insoluble in alkali insoluble in alcohol & ether.
3) Pungent smell.
4) On heating HN_3 decomposed to N_2 & H_2.
5) On reaction with HCl and HI, HN_3 decomposes to NH_3, N_2 and X_2. (X = Cl or I)
6) HN_3 undergoes reduction to NH_3 or N_2H_4 in presence of Na & Hg.

$$HN_3 + 4H_2 \rightarrow 3NH_3$$
$$2NH_3 + 5H_2 \rightarrow 2N_2H_4$$

7) HN_3 undergoes oxidation to N_2 in presence of oxidizing agents like HNO_2, HOCl, $KMnO_4$.

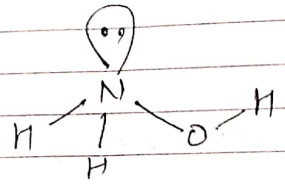
a) $HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O$

b) $HN_3 + HOCl \rightarrow 3N_2 + HCl + H_2O$

c) $10\,HN_3 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 15N_2$

HYDROXYL AMINE (NH_2OH)

Structure:



Trigonal pyramidal shape wher N-atom is sp^3 hybridized, and one sp^3 hybrid orbitals. contains a lone pair of $e^{\ominus}$ and remaining three are singly filled sp^3 hybrid orbitals forming N-H, N-H and N-OH bonds.

PROPERTIES of Hydroxylamine NH_2OH

1) White crystalline solid with mpt = 33°C. and bpt 58°C.
2) NH_2OH undergoes ~~disproportionation~~ explosion on heating.

$$4NH_2OH + O_2 \xrightarrow{\Delta} 2N_2 + 6H_2O$$

3) Reaction with HNO_2 leads to formation of Nitrous oxide

$$NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O$$

Illy it reacting with HNO_3 forms nitric oxide.

$$NH_2OH + HNO_3 \rightarrow 2NO + 2H_2O.$$

4) Reaction of NH_2OH with aldehyde or ketone form oxime

$$R_2C=O + NH_2OH \rightarrow R_2C=NOH.$$

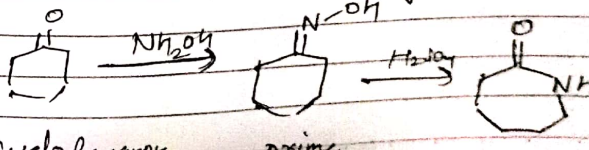
Oxime

5) NH_2OH undergoes reduction in presence of Zn/HCl to form amines or ammonia.

$$NH_2OH \xrightarrow{Zn/HCl} NH_3.$$

USES.

a) Hydroxyl amine and its salts are commonly used as reducing agents.
b) Can also act as antioxidants for fatty acids.
c) In synthesis of Nylon 6, cyclohexanone is converted to its oxime using NH_2OH



cyclohexanon oxime

which is later on converted to caprolactum by treatment with acid.