Greenwood & Earnshaw

2nd Edition

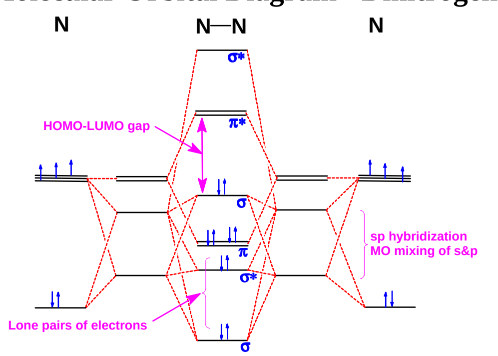
Chapter 11

Nitrogen

Dinitrogen

- N≡N is chemically very unreactive, mp –210°C, bp –195.8°C its great bond strength, ΔH_{diss} = 945.41 kJ/mol, $d_{N\text{-}N}$ = 109.76 pm, and great thermodynamic stability causes many nitrogen compounds to be endothermic.
- The N_2 lone pairs are very low in energy and are much less available for donation than the isoelectronic CO.
- The π* molecular orbitals are very high in energy (π bonds are very strong) and π-backbonding is less favored.
- A large HOMO-LUMO energy gap makes it hard to promote electrons or reduce dinitrogen.
- Dinitrogen is a non-polar molecule. isoelectronic with: CO, NO^+, CN^-, C_2^{2-}, and similar to HC_2^-, H_2C_2.

Molecular Orbital Diagram - Dinitrogen



Note the two π-bonds are stronger than the σ-bond due to bond compression.

Reactions of Dinitrogen

Nitrides and nitrogen oxides:

$$6\,Li + N_2 \xrightarrow{25°C} 2\,Li_3N$$

Many small metals (Mg, Al, Ti) react with dinitrogen at elevated temperatures.

$$N_2 + O_2 \xrightarrow{\Delta,\ h\nu,\ elec.\ dis.} NO_x$$

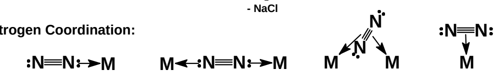
Dinitrogen "fixation" during electrical storms and high temperature combustion contributes to soil fertility & "acid rain."

Dinitrogen coordinates to some metal complexes:

$$[Ru(NH_3)_5(H_2O)]^{2+} + N_2 \longrightarrow [Ru(NH_3)_5(N_2)]^{2+} + H_2O$$

$$[MoCl_4(PMe_2Ph)_2] + 2\,N_2 \xrightarrow[PMe_2Ph,\ -NaCl]{toluene,\ Na/Hg} cis\text{-}[Mo(N_2)_2(PMe_2Ph)_2]$$

Dinitrogen Coordination:



η1 most common | bis-η1 impt in fixation | μ-bis-η2 | η2 rare

Nitrides – Nitrido Complexes

^{14}N 99.634%, I = 1 ^{15}N 0.366%, I = $^{1}/_{2}$

Ionic: $3\,Ca + N_2 \longrightarrow Ca_3N_2$ also Li, Mg, Zn, Ti other small cations.

$$Al_2O_3 + N_2 + C_x \longrightarrow 2AlN + 3\,CO$$

Covalent: Si_3N_4 Network covalent - with alumina in hi tech ceramics.

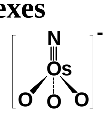
S_4N_4, P_3N_5 } Molecular, all have some type of dπ-pπ bonding.

Metallic: Transition metals (Zr, Ti, Cr) in cubic and hexagonal close packed littices, N fits into octahedral sites.

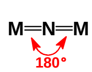
Nitrides – Nitrido Complexes

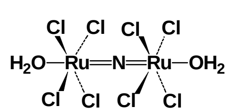
Nitrido:

$$OsO_4 + NH_3 \longrightarrow H_3O^+$$

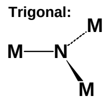


Linear:



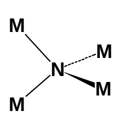


Trigonal:



$[NIr_3(SO_4)_6(H_2O)_3]^{4-}$

Tetrahedral:

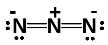


$[N(HgMe)_4]^+$

Azides – Azido Compounds

Ionic Azides:

N_3^-

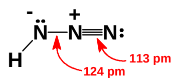


isoelectronic with O=C=O

$d_{N=N}$ = 116 pm

Ionic azides are stable, the ion is symmetrical, the alkali metal salts are commercially available.

Covalent Azides: HN_3, RN_3, $Pb(N_3)_2$, HgN_3



Hydrazoic acid, pKa = 4.77, pungent, revolting odor, very toxic. Concentated and anhydrous acids are explosive.

ΔH_f° = 269.5 kJ/mol ΔG_f° = 327.2 kJ/mol

A very energetic molecule, heavy metal salts are used as detonators for explosives, not hygroscopic, reliable.

Hydrides

Ammonia: NH_3 $K_b = 1.8 \times 10^{-5}$ NH_4^+

Largest industrial commodity on a molar basis.

$RBr + NH_3 \longrightarrow RNH_3^+ Br^- \xrightarrow{OH^-,\ RBr,\ OH^-,\ RBr,\ OH^-,\ RBr} R_4N^+ Br^-$

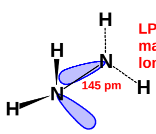
$\downarrow Ag_2O.H_2O$

$R_4N^+ OH^-$

Ammonia and amines are weak bases ammonium ions are weak acids. Tetraalkylammonium hydroxide is a strong base.

Hydrazine: H_2NNH_2 $K_b = 8.5 \times 10^{-7}$ $H_2NNH_3^+$

$K_b = 8.9 \times 10^{-16}$ $^+H_3NNH_3^+$ A strong acid

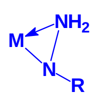


LP-LP repulsions make the N-N bond long and weak.

gauche conformation torsion angle 90°-95°

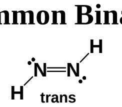
1e,2e,4e reducing agent, stronger in base than acid.
1e E°_{red} = -1.74 V acid
1e E°_{red} = -2.42 V base

Hydrazide Ligand:

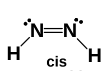


Less Common Binary Hydrides

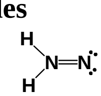
Diazine: HNNH



trans
more stable

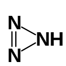


cis
not stable
Ligand important in nitrogen fixation.



1,1-isomer

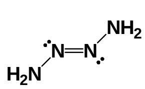
Cyclotriazene: (triaziridine)



Triazane: H_2NNHNH_2 (aminohydrazine)

Tetrazane: $H_2NNHNHNH_2$ (diaminohydrazine)

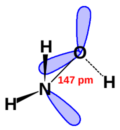
trans-2-tetrazene



Several "binary hydrides" can be made such as ammonium and hydrazinium azide salts; dimers and trimers of hydrazoic acid or triaziridine.

Hydroxylamine & Nitrogen Fixation

Hydroxylamine: H_2NOH Kb = 6.6 X 10^{-9} H_3NOH^+

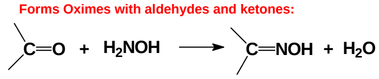


Trans conformation in the crystal

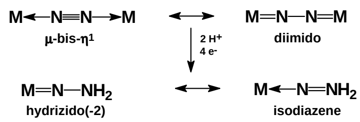
Made by the reduction of ammonium nitrite in a gel using aqueous bisulfate/sulfur dioxide, Raschig Synthesis.

Industrially used as reducing agent, absorbent for nitrogen oxides.

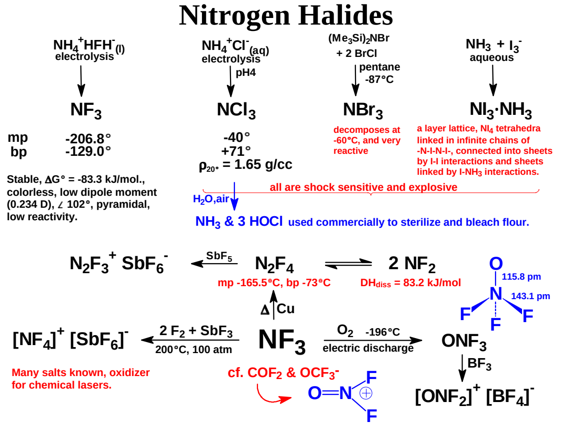
Forms Oximes with aldehydes and ketones:



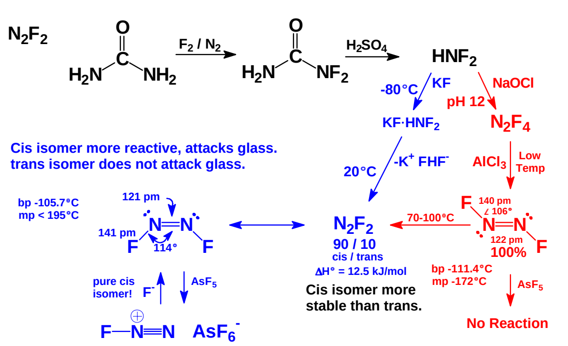
Nitrogen Fixation:



Nitrogen Halides

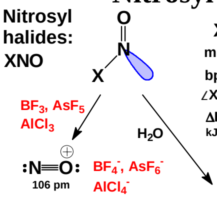


Nitrogen Halides



Nitrosyl & Nitryl Halides

Nitrosyl halides: XNO

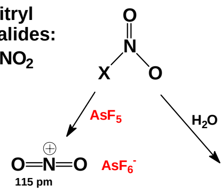


X	F	Cl	Br
mp°C	-132.5	-59.6	-56
bp°C	-59.9	-6.4	~0
∠XNO	110	113	117
ΔH°$_f$ kJ/mol	-66.5	+51.7	+82.2

$3\ HNO_2 \longrightarrow HNO_3 + 2\ NO + H_2O$

{HOX, HNO} ⟶ HX + HNO$_2$ — Potent solvents for dissolving metals.

Nitryl halides: XNO$_2$

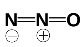


X	F	Cl
mp°C	-166	-145
bp°C	-72.5	-15.9
∠XNO	118	115
ΔH°$_f$ kJ/mol	-80	+13

{HOX, HNO$_2$} ⟶ HX + HNO$_2$

Oxides of Nitrogen

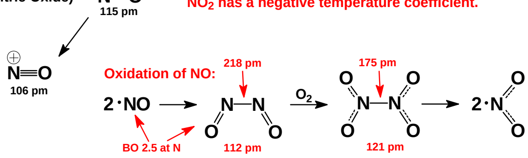
Dinitrogen Monoxide: (Nitrous Oxide) N_2O



Isoelectronic with carbon dioxide & NO_2^+. Very unreactive, very stable gas, anesthetic (laughing gas), greenhouse gas $t_{1/2}$ = 115 year "lifetime." Natural source, microbial degradation of NH_4NO_3.

Nitrogen Monoxide: (Nitric Oxide) N≡O 115 pm

A stable free radical, paramagnetic, colorless, bp - 151.8°C, little tendency to dimerize. Oxidation to NO_2 has a negative temperature coefficient.

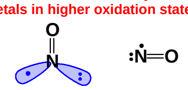


Nitric Oxide as a Ligand – Bent Nitrosyls

Linear: NO$^+$ — A 3 electron donor, 2 NO's will replace 3 CO's in an EAN complex.

M—N—O ∠ 170-180° — νNO = 1650-1900 cm^{-1}. Common with early transition metals and middle transition metals in higher oxidation states.

Bent:



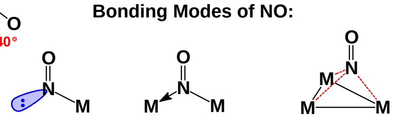
Gp A: (2 electron donor)

M—N—O ∠ 140-170° — νNO = 1500-1690 cm^{-1}. Common with late transition metals and middle transition metals in lower oxidation states.

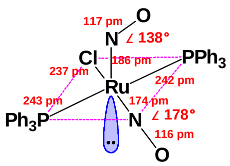
Gp B: (1 electron donor) NO$^-$

M—N—O ∠ 120-140°

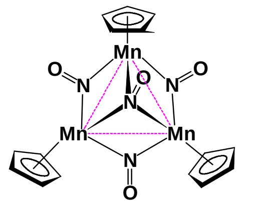
Bonding Modes of NO:



Nitric Oxide as a Ligand



$[RuCl(NO)_2(PPh_3)_2]^+$



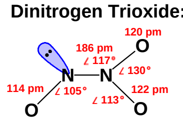
$[\{(\eta^5\text{-}C_5H_5)Mn\}_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NO)]$

Oxides of Nitrogen

Dinitrogen Trioxide: $N_2O_3 \rightleftharpoons NO + NO_2$

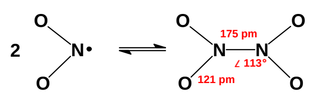
NO: colorless; NO_2: red-brown

mp -100.1°C; mixed dimer



Light blue solid, intense blue liquid, turns green as NO_2 dissociates, color becomes less intense.

Nitrogen Dioxide & Dinitrogen Tetroxide



ΔH_{diss} = +57.20 kJ/mol
ΔG_{diss} = +4.77 kJ/mol
$\Delta S°$ = 175.7 J/K·mol

Isoelectronic with B_2F_4 & $C_2O_4^{2-}$ whose C-C and B-B bonds are of normal length. Does not autoionize, but ionic intermediates form in high dielectric solvents. An intermediate in the production of nitric acid.

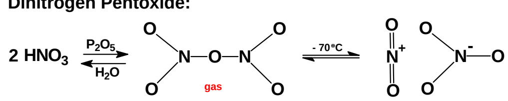
Nitric Acid:

$NH_3 \xrightarrow[O_2]{Pt} NO \xrightarrow{O_2} N_2O_4 \xrightarrow{H_2O} HNO_3 + HNO_2$

$3\ HNO_2 \longrightarrow H_3O^+\ NO_3^- + 2\ NO$ (to be recycled)

Oxides of Nitrogen

Dinitrogen Pentoxide:



Structure poorly understood

Ionic solid

Oxoacids – Oxoanions:

Hyponitrous Acid - Hyponitrite

HON═NOH

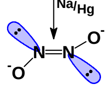
pK_a = 6.9 ; 11.6

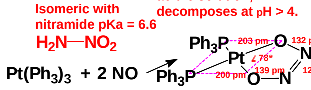
Isomeric with nitramide pKa = 6.6

$H_2N—NO_2$

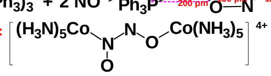
Weak dibasic acid of unknown structure. Stable for weeks in acidic solution, decomposes at pH > 4.

$NaNO_3$ or $NaNO_2$ $\xrightarrow{Na/Hg}$



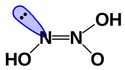


Salts are stable, reducing, *"trans"* by vibrational spect. *"Cis"* ion known as a ligand. Many "non-EAN" nitrosyls are *cis*-hyponitrites.

also: 

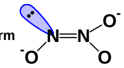
Oxoacids – Oxoanions

Hyponitric Acid - Hyponitrates:



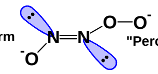
Acid is known only in solution and is explosive.

α form



$Na_2N_2O_3$ Angeli's Salt

β form



"Peroxohyponitrite"

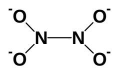
$$Na_2N_2O_2 \xrightarrow[\text{fast}]{N_2O_{4(l)}} \beta\text{-}N_2O_3^{2-} \xrightarrow{\text{slow}} N_2O_5^{2-} \xrightarrow[100\,°C]{\text{slow}} N_2O_6^{2-}$$

$$\alpha\text{-}N_2O_3^{2-} \longrightarrow N_2O_4^{2-} \longrightarrow N_2O_6^{2-}$$

Nitroxylic (Hydronitrous) Acid - Nitroxolate Anion:

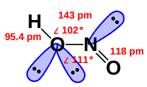
"Acid Explosive"

$$2\ NaNO_2 + 2\ Na \xrightarrow{NH_{3(l)}}$$



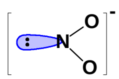
Oxoacids – Oxoanions

Nitrous Acid - Nitrites

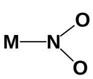


planar

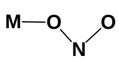
45 kJ/mol barrier to rotation



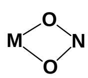
nitrite is a very versatile ligand



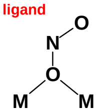
nitro



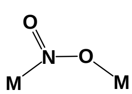
nitrito



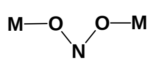
chelating



O-bridging



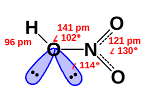
cis-unsymmetrical
N,O bridging -- *trans*??



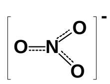
not definitely established

Oxoacids – Oxoanions

Nitric Acid - Nitrates



Almost planar gas, $\angle_{HON}$ torsion 2° bp 82.6°C. Nitric Acid will form H-bonded complexes with nitrate.

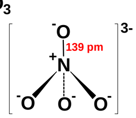


The nitrate ligand may coordinate in a manner similar to nitrite and may use all three oxygen atoms.

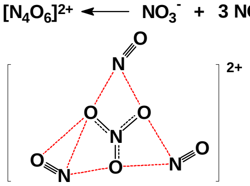
Orthonitrate: H_3NO_4 unknown

$$[N_4O_6]^{2+} \longleftarrow NO_3^- + 3\ NO^+$$

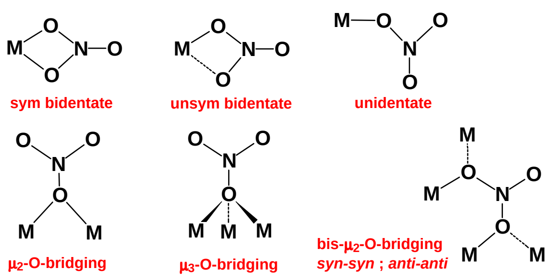
$$Na_2O + NaNO_3 \xrightarrow{\text{fuse}} Na_3NO_4$$



Tetrahedral anion, very short N-O bond due to strong polar interactions.



Coordination Modes of Nitrate Ligand



Many metal nitrates melt at "low" temperatures without decomposition
$LiNO_3$ (255°C); $CsNO_3$ (419°C); $AgNO_3$ (212°C).