Diazonium salts and Nitro compounds

DIAZONIUM SALTS

The diazonium salts have general formula \( R^+N_2X^- \) where \( R \) stands for aryl and \( X^- \) ion may \( Cl^- \), \( Br^- \), \( HSO_4^- \), \( BF_4^- \) etc

NOMENCLATURE

Arenediazonium salts are named by adding the suffix diazonium to the name of parent aromatic hydrocarbon Example:

\[
\begin{align*}
\text{Benzenediazonium chloride} \\
\text{p-toluenediazonium hydrogen sulphate} \\
p\text{-nitrobenzene diazonium fluoroborate}
\end{align*}
\]

STABILITY OF DIAZONIUM SALT

Aryldiazonium salts are stable because of dispersal of positive charge over benzene ring due to resonating structures.
PREPARATION OF ARENEDIAZONIUM CHLORIDE

- This process of converting an aromatic primary amine into diazonium salt is called diazotization.
- Diazotisation should be carried out at low temperature since at higher temperature benzenediazonium salt reacts with water to form phenol.

\[
\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \rightarrow \text{N}_2\text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O}
\]

- Aromatic amines substituted with electron withdrawing groups require more concentrated acids than unsubstituted amines because of their weak basic character.

Mechanism:
\[
\text{NaNO}_2 + \text{HCl} \rightarrow \text{HNO}_2 + \text{NaCl}
\]
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PHYSICAL PROPERTIES
- Aryl diazonium salts are colourless crystalline solids which turn brown when come in contact with air
- They are highly soluble in water but sparingly soluble in ethanol and insoluble in ether
- They are unstable and decomposes easily when dry

CHEMICAL PROPERTIES
A) Replacement reactions: The reactions in which the diazonium group (-N2X) as a whole is replaced by monovalent atom or group
1. Replacement by hydrogen
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2. Replacement by hydroxyl group

\[
\begin{align*}
\text{N}_2\text{BF}_4 + \text{C}_6\text{H}_5\text{OH} & \xrightarrow{\text{Zn, } \Delta} \text{C}_6\text{H}_5\text{OH} \\
\text{N}_2\text{HSO}_4^- + \text{H}_2\text{O} & \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 + \text{N}_2
\end{align*}
\]

Highly acidic conditions avoid chances of coupling reaction between phenol and diazonium salt.

3. Replacement by halogen

(i) Sandmeyer reaction

\[
\begin{align*}
\text{N}_2\text{Cl}^- + \text{C}_6\text{H}_4\text{NO}_2^- & \xrightarrow{\text{CuCl/Cl}_2} \text{C}_6\text{H}_4\text{Cl}^- + \text{N}_2 + \text{HCl} \\
\text{N}_2\text{Cl}^- & \xrightarrow{\text{CuBr/Br}_2} \text{C}_6\text{H}_4\text{Br}^- + \text{N}_2 + \text{HBr}
\end{align*}
\]

(ii) Gattermann reaction

\[
\begin{align*}
\text{N}_2\text{Cl}^- + \text{C}_6\text{H}_4\text{NO}_2^- & \xrightarrow{\text{Cu/Cl}_2} \text{C}_6\text{H}_4\text{Cl}^- + \text{N}_2 \\
\text{N}_2\text{Cl}^- & \xrightarrow{\text{Cu/Br}_2} \text{C}_6\text{H}_4\text{Br}^- + \text{N}_2
\end{align*}
\]
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(iii) Replacement by iodine

\[
\begin{align*}
\text{N}_2\text{Cl}^- + \text{KI} & \rightarrow \text{N}_2 + \text{KCl} + \text{I}^- \\
\text{Iodobenzene}
\end{align*}
\]

(iv) Replacement by fluorine (Balz–Schiemann reaction)

\[
\begin{align*}
\text{N}_2\text{Cl}^- + \text{HBF}_4^- & \rightarrow \text{N}_2\text{BF}_4^- + \text{HCl} \\
\text{Δ} & \rightarrow \text{N}_2 + \text{BF}_3 + \text{C}_6\text{H}_5
\end{align*}
\]

4. Replacement by \((-\text{NO}_2\)) group

\[
\begin{align*}
\text{N}_2\text{Cl}^- + \text{HBF}_4^- & \rightarrow \text{N}_2\text{BF}_4^- + \text{HCl} \\
\text{NaNO}_2 / \text{Cu} & \rightarrow \text{N}_2 + \text{NF}_3 + \text{NaBF}_4
\end{align*}
\]

5. Replacement by cyano \((-\text{CN}\)) group

\[
\begin{align*}
\text{N}_2\text{Cl}^- + \text{CuCN} & \rightarrow \text{CN}^- + \text{CuCl} + \text{N}_2
\end{align*}
\]

6. Replacement by aryl group (Gomberg Bachmann reaction)

\[
\begin{align*}
\text{N}_2\text{Cl}^- + \text{Br} + \text{NaOH} & \rightarrow \text{o-bromodiphenyl}
\end{align*}
\]
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B) Coupling reactions: The reactions in which both the nitrogen atoms are retained and only halogen is replaced

1. Reduction

\[
\text{ benzene } + 4 \text{ [H]} \xrightarrow{\text{SnCl}_2/\text{HCl}} \text{ benzene} \xrightarrow{\text{NaOH}} \text{ benzene} + \text{N}_2 \text{Cl}^- + \text{H}_2\text{O} \]

2. Coupling reaction

\[
\text{ benzene } + \text{ benzene} \xrightarrow{\text{p-hydroxyazobenzene}} \text{ benzene} \xrightarrow{\text{p-amino azobenzen}} + \text{Cl} + \text{H}_2\text{O} \]

Mechanism

\[
\text{ Diazonium ion} \]

\[
\text{ Diazonium ion} \]

\[
\text{ Diazonium ion} \]

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\text{ Diazonium ion} \]

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\text{ Diazonium ion} \]

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\text{ Diazonium ion} \]

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\text{ Diazonium ion} \]
NITRO COMPOUNDS

- When nitro group is attached to an alkyl group the compounds are known as nitro-alkanes and nitro group attached to aryl group are known as nitroarenes

- Nitro compounds are classified as primary, secondary and tertiary depending upon whether the nitro group is attached to a primary, secondary or tertiary carbon respectively

```
R - C - NO₂       R - C - NO₂       R - C - NO₂
  H            H               R
```

primary nitroalkane  secondary nitroalkane  tertiary nitroalkane
Diazonium salts and Nitro compounds

STRUCTURE OF $-\text{NO}_2$ GROUP

$\begin{align*}
\text{NO}^- & \leftrightarrow \text{NO}_2^- \\
\text{OR} & \\
\text{NO} & \leftrightarrow \text{NO}_2
\end{align*}$

PREPARATION OF NITRO COMPOUNDS

1. Nitration

$$\begin{align*}
\text{CH}_4 + \text{NHO}_3 & \xrightarrow{400^\circ\text{C}} \text{CH}_3\text{NO}_2 + \text{H}_2\text{O} \\
\text{nitromethane} & \\
\text{CH}_3 - \text{CH}_3 + \text{NHO}_3 & \xrightarrow{400^\circ\text{C}} \begin{cases} \text{CH}_3 - \text{CH}_2 - \text{NO}_2 & \text{nitroethane (73\%)} \\ \text{CH}_2\text{NO}_2 & \text{nitromethane (27\%)} \end{cases}
\end{align*}$$

Mechanism

$$\begin{align*}
\text{HO} + \text{NO}_2 & \rightarrow \text{HO} + \text{NO}_2 \\
\text{R} - \text{H} + \text{NO}_2 & \rightarrow \text{R-NO}_2 + \text{H} \\
\text{OH} + \text{H} & \rightarrow \text{H}_2\text{O}
\end{align*}$$

Ease of substitution follows the order tertiary > secondary > primary
2. From alkyl halides

\[
R - Br + AgNO_2 \xrightarrow{\text{alcohol}} R-NO_2 + AgBr
\]

- If we use sodium nitrate (NaNO_2) in place of AgNO_2 in the above reaction, then alkyl nitrite is obtained as major yield.

**Reason**

Nitrite ion is an ambidient nucleophile. Silver nitrite being covalent compound attacks electrophilic carbon of alkyl halide through a lone pair. Since nitrogen is less electronegative than oxygen, its lone pair is easily available for bonding.

But sodium nitrite is an ionic compound with negative charge on oxygen.

- Order of reactivity of alkyl halides towards nitroalkane formation is Primary > secondary > tertiary.
- Order of reactivity of alkyl halides towards nitrite formation is Tertiary > secondary > primary.
Diazonium salts and Nitro compounds

3. Oxidation of aromatic amine

\[ \text{NH}_2 \xrightarrow{\text{CF}_3\text{CO}_3\text{H}} \text{NO}_2 \]

4. From diazonium salts

\[ \text{N}_2\text{Cl} \xrightarrow{\text{CF}_3\text{CO}_3\text{H}} \text{NO}_2 + \text{HCl} + \text{N}_2 \]

PHYSICAL PROPERTIES

- Nitroalkanes are colourless, pleasant smelling liquids, whereas nitroarenes are pale yellow crystalline solids except nitrobenzene. Which is pale yellow liquid with an odour of bitter almond
- Both nitroalkanes and nitroarenes are insoluble in water but fairly soluble in organic solvents
- Being highly polar in nature, nitroalkanes and nitroarenes possess strong dipole-dipole interactions. Hence they have much higher boiling points than hydrocarbons of comparable molecular masses

CHEMICAL PROPERTIES

1. Reduction

\[ \text{R - NO}_2 \xrightarrow{\text{H}_2\text{O}, \text{[H]}} \text{R - N = O} \]

Nitroso compound

\[ \text{R - NH}_2 \xrightarrow{\text{H}_2\text{O}, \text{[H]}} \text{R - NHOH} \]

Substituted hydroxy amine
Diazonium salts and Nitro compounds

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{NO}_2 & \xrightarrow{\text{Sn} / \text{HCl, acidic medium}} \text{CH}_3\text{CH}_2\text{-NH}_2 \\
\text{CH}_3\text{CH}_2\text{NO}_2 & \xrightarrow{\text{Zn} / \text{NH}_4\text{Cl}, \text{H}_2\text{O, neutral medium}} \text{CH}_3\text{CH}_2\text{-NHOH + ZnO, N-ethyl hydroxylamine} \\
\text{CH}_3\text{CH}_2\text{NO}_2 & \xrightarrow{\text{Pd/C, ethanol, catalytic reduction}} \text{CH}_3\text{CH}_2\text{-NH}_2 \\
\text{CH}_3\text{CH}_2\text{NO}_2 & \xrightarrow{\text{LiAlH}_4, \text{ether}} \text{CH}_3\text{CH}_2\text{-NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{Fe/HC1 or Sn/HCl, acidic medium} & \xrightarrow{} \text{NH}_2 \\
\text{Zn/NH}_4\text{Cl, H}_2\text{O, neutral medium} & \xrightarrow{} \text{N-phenyl hydroxylamine} \\
\text{Zn/NaOH, CH}_3\text{OH, alkaline medium} & \xrightarrow{} \text{Azoxybenzene}
\end{align*}
\]
2. Hydrolysis

\[ \text{R - CH}_2\text{-NO}_2 + \text{H}_2\text{O} \xrightarrow{\text{HCl or H}_2\text{SO}_4} \text{RCOOH} + \text{NH}_2\text{OH} \]

- carboxylic acid
- hydroxylamine

\[ 2\text{R}_2\text{CHNO}_2 \xrightarrow{\Delta} 2\text{R}_2\text{CO} + \text{N}_2\text{O} + \text{H}_2\text{O} \]

- ketone
- nitrous oxide

3. Reaction with nitrous acid

\[ \text{CH}_3\text{-CH}_2\text{-NO}_2 + \text{O} = \text{N} - \text{O} - \text{H} \]

\[ \text{CH}_3\cdot\text{C} - \text{NO}_2 + \text{NaOH} \rightarrow \text{NONa} \]

- sodium nitroate (red)
Tertiary nitroalkanes do not react with HNO$_2$, as they lack $\alpha$-hydrogen atom

This is also known as Victor Meyer’s test for distinction of 1°, 2° and 3° nitroalkanes

4. Reaction with Grignard reagent.

5. Electrophilic substitution reaction
6. Nucleophilic substitution reaction
7. Action of heat

\[ \text{RCH}_2 - \text{CH}_2 - \text{NO}_2 \xrightarrow{300^\circ C} \Delta \text{RCH} = \text{CH}_2 + \text{NO}_2 \]

On strong heating they decompose with violence

\[ 2\text{CH}_2 - \text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{CO}_2 + 3\text{H}_2 \]

**CYANIDES AND ISOCYANIDES**

- Cyanides and isocyanides are isomeric to each other and are considered as derivative of two tautomeric forms of hydrogen cyanides
  
  \[
  \begin{align*}
  \text{H - C} & \equiv \text{N} \\
  \text{cyanide form} & \\
  \text{H} & \equiv \text{N - C} \\
  \text{isocyanide form}
  \end{align*}
  \]

- \(-\text{CN}\) can attach either through carbon or nitrogen atom. Such a group which has more than one attacking sites is known as ambidient group

**STRUCTURE OF \(-\text{CN}\) or \(-\text{NC}\) group**

ORBITAL STRUCTURE OF ALKYL CYANIDES
GENERAL METHOD OF PREPARATION OF CYANIDES

1. From alkyl halide
   \[ R - X + \text{NaCN (alc.)} \rightarrow R - \text{CN} + \text{NaX} \]
   Aryl cyanides cannot be prepared by this method, since Ar-X bond is not easy to be cleaved by CN⁻.
   For preparing aryl cyanides, aryl halides are heated with anhydrous cuprous cyanide at 200°C in the presence of pyridine.

   \[
   \begin{align*}
   \text{Br} + \text{Cu}_2(\text{CN})_2 \text{pyridine} & \xrightarrow{200^\circ C} 2 \text{CN} + 2 \text{CuBr} \\
   \end{align*}
   \]

2. From acid amides
   \[
   R - \text{C} - \text{NH}_2 \xrightarrow{P_2\text{O}_5, \Delta} R - \text{C} \equiv \text{N} + \text{H}_2\text{O}
   \]

3. From Grignard reagent
   \[
   \text{RMgX} + \text{Cl} - \text{CN} \rightarrow R - \text{CN} + \text{MgCl}
   \]
Diazonium salts and Nitro compounds

4. From carboxylic acid

\[ \text{RCOOH} + \text{NH}_3 \xrightarrow{\text{Al}_2\text{O}_3, 250^\circ\text{C}} \text{RCOONH}_4 \]
\[ \xrightarrow{\text{Al}_2\text{O}_3, 500^\circ\text{C}} \text{R} - \text{CN} \]

5. From arene diazonium salts

\[ \overset{+}{\text{N}} \equiv \overset{-}{\text{NCl}} \overset{\text{CuCN}}{\xrightarrow{\text{CuCN or Cu powder}}} \overset{+}{\text{C}} \]

6. From sodium salt of carboxylic acid

\[ \text{RCOONa} + \text{Br} - \text{CN} \xrightarrow{\Delta} \text{R} - \text{CN} + \text{CO}_2 + \text{NaBr} \]

GENERAL METHOD OF PREPARATION OF ISOCYANIDES

1. From alkyl halides

\[ \text{R} - \text{X} + \text{AgCN (alco.)} \rightarrow \text{R} - \text{N} \equiv \overset{+}{\text{C}} + \text{AgX} \]

- AgCN is covalent in nature. Only nitrogen atom has lone pair of electrons available for nucleophilic attack, thus attack takes place mainly through nitrogen atom leading to formation of isocyanide along with small amount of cyanide

\[ \text{Ag} - \overset{+}{\text{C}} \equiv \overset{+}{\text{N}} + \text{R} - \text{X} \rightarrow \text{R} - \text{N} \equiv \overset{+}{\text{C}} + \text{AgX} \]

2. Carbylamine reaction

\[ \text{R} - \text{NH}_2 + \text{CHCl}_3 + 3\text{KOH (alc.)} \xrightarrow{\Delta} \]

\[ \text{R} - \text{N} \equiv \overset{+}{\text{C}} + 3\text{KCl} + 3\text{H}_2\text{O} \]

\[ \overset{+}{\text{NH}_2} + \text{CHCl}_3 + 3\text{KOH (alc.)} \xrightarrow{\Delta} \overset{\text{phenyl isocyanide}}{\overset{+}{\text{C}} \equiv \overset{+}{\text{N}}} + 3\text{KCl} + 3\text{H}_2\text{O} \]
Diazonium salts and Nitro compounds

3. From N-alkyl formamides

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{N} \quad \text{R} \\
& \quad \Delta \quad \text{POCl}_3 \quad \text{pyridine}
\end{align*}
\]

\[ R \quad \text{\( \overset{\equiv}{\text{C}} \) + H}_2\text{O} \]

PHYSICAL PROPERTIES OF CYANIDES AND ISOCYANIDES

1. Physical state and smell:
   Lower members of alkyl cyanides and isocyanides are colourless liquids whereas higher members are crystalline solids.
   Alkyl cyanides are pleasant smelling, while alkyl isocyanides have extremely unpleasant smell.

2. Solubility
   Lower member of alkyl cyanide are sparingly soluble in water due to intermolecular hydrogen bonding, but the solubility decreases with increase of molecular weight.
   However isocyanides (both alkyl and aryl) and aryl cyanides are insoluble in water. All members of cyanides and isocyanides are fairly soluble in organic solvents.

3. Boiling points
   Both \(-\text{CN}\) and \(-\text{NC}\) group are polar in nature hence they possess strong intermolecular dipole-dipole interaction.
   As a result of which they have higher boiling point than that of alkyl halides or hydrocarbons of comparable molecular mass.
   However boiling points of alkyl isocyanides are lower than that of alkyl cyanides since \(-\text{NC}\) group is less polar than \(-\text{CN}\) group.

CHEMICAL PROPERTIES OF CYANIDES AND ISOCYANIDES

(A) Chemical reactions shown by cyanides only

1. Basic nature of cyanides
   Inspite of the presence of unshared pair of electrons on nitrogen atom, the nitriles or cyanides are not enough basic to form salt with aqueous acids.
   Because in nitriles, nitrogen atom is sp-hybridised and hence highly electronegative. Electron pair present in sp-orbitals are less easily available for donation and hence nitriles behave as weak base, weaker than amines and ammonia.
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(2) Reaction with Grignard reagent

\[ R - C = N + R'MgX \rightarrow R' - C = N\text{MgX} \]

\[ \text{H}_2\text{O} / \text{H}^+ \]

\[ \text{NH}_3 + R - C = O + \text{Mg(OH)}X \]

(3) Reaction with alcohol

\[ R - C \equiv N + R'OH + \text{HCl} \rightarrow R - C \cdot \text{OR'}^{\text{Cl}^{-}} \]

\[ \text{Imido ester} \]

\[ \text{NH}_4\text{Cl} + R - C - \text{OR'} \]

(4) Addition reactions

\[ \text{CH}_3 - C \equiv N + \text{HCl} \rightarrow \text{CH}_3 - C \equiv \text{NH} \]

\[ \text{imino chloride} \]

\[ \text{CH}_3 - C \equiv N + \text{NH}_3 \rightarrow \text{CH}_3 - C = N^{\text{NH}_3} \]

\[ \text{Arildines} + \text{NH}_2 \]

\[ \text{CH}_3 - C \equiv N + R'\text{NH}_2 \rightarrow \text{CH}_3 - C \equiv \text{NHR'} \]

\[ \text{substituted arildines} \]

\[ \text{CH}_3 - C \equiv N + \text{H}_2\text{S} \rightarrow \text{CH}_3 - C - \text{NH}_2 \]

\[ \text{thioacetamide} \]
Diazonium salts and Nitro compounds

(B) Chemical reaction shown by isocyanides only

1. 
\[
\text{CH}_3 - \text{N} \equiv \text{C}^- + \text{Cl}_2 \rightarrow \text{CH}_3 - \text{N} = \text{C} = \text{Cl}
\]

\[
\text{CH}_3 - \text{N} \equiv \text{C}^- + \text{S} \rightarrow \text{CH}_3 - \text{N} = \text{C} = \text{S}
\]

- methyl isothiocyanate

2. Reaction shown by both cyanides and isocyanides

(a) Hydrolysis of cyanides: complete hydrolysis

\[
\begin{align*}
\text{R - C} \equiv \text{N} &\xrightarrow{\text{H}_2\text{O}} \text{R - C} \equiv \text{NH}_2 \\
&\xrightarrow{\text{H}_2\text{O}} \text{R - C} \equiv \text{OH} + \text{NH}_4^+
\end{align*}
\]

Partial hydrolysis

\[
\text{R - C} \equiv \text{N} + \text{H}_2\text{O} \xrightarrow{\text{conc. HCl or conc. H}_2\text{SO}_4} \text{R - C} \equiv \text{NH}_2
\]

(b) Hydrolysis by isocyanide.

\[
\text{R - N} \equiv \text{C} + 2\text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{R-NH}_2 + \text{HCOOH}
\]

(2) Reduction

(a) Complete reduction
Diazonium salts and Nitro compounds

\[ R - C \equiv N + 2H_2 \xrightarrow{Ni \ or \ Pt} R - CH_2 - NH_2 \]
\[ 1^\circ \ \text{amine} \]

\[ R - N \equiv C + 2H_2 \xrightarrow{Ni \ or \ Pt} R-NH - CH_3 \]
\[ 2^\circ \ \text{amine} \]

(b) Partial reduction

\[ R - C = N \xrightarrow{SnCl_2 / HCl} [ R - CH = NH \cdot HCl ] \xrightarrow{H_2O} RCHO + NH_4Cl \]
\[ \text{imine hydrochloride} \]

\[ \text{bezaldinine hydrochloride} \]

\[ \text{benzaldehyde} \]