Cyanides and Isocyanides

Hydrogen cyanide is known to exist as a tautomeric mixture.

 $\mathsf{H} - \mathsf{C} \equiv \mathsf{N} \rightleftharpoons H - N \quad C \quad \geqq$

Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.

$$\begin{array}{c} R-C\equiv N\\ AlkylCyanide \end{array} \qquad \qquad \begin{array}{c} R-N\\ Alkylisocyanide \end{array} \qquad \qquad \begin{array}{c} \rightleftharpoons\\ \end{array}$$

Nomenclature: According to IUPAC system, cyanides are named as "alkane nitriles". In naming the hydrocarbon part, carbon of the – CN group is also counted.

Formula	As cyanide	IUPAC name
CH₃CN	Methyl cyanide(Acetonitrile)	Ethane nitrile
C_2H_5CN	Ethyl cyanide(Propiononitrile)	Propane nitrile
C ₃ H ₇ CN	Propyl cyanide	Butane nitrile
C₄H ₉ CN	Butyl cyanide	Pentane nitrile

Iso cyanides are named as "Alkyl carbylamine" or "Carbyl amino alkane".

Formula	As isocyanide(Comman name)	IUPAC name
CH₃NC	Methyl isocyanide (Methyl isonitrile)	Methyl carbylamine (Carbylamino methane)
C_2H_5NC	Ethyl isocyanide (Ethyl isonitrile)	Ethyl carbylamine (Carbylamino ethane)
C ₃ H ₇ NC	Propyl isocyanide (Propyl isonitrile)	Propyl carbylamine (Carbylamino propane)

(1) Alkyl Cyanides

(i) Methods of preparation

(a) From alkyl halides: The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.

$$\begin{array}{c} RX + KCN(orNaCN) \rightarrow RCN \\ \text{Alkyl} \\ \text{halide} \end{array} + \begin{array}{c} RNC \\ \text{Isonitrile} \\ (Major product) \end{array} + \begin{array}{c} RNC \\ \text{Isonitrile} \\ (Minor product) \end{array}$$

(b) From acid amides:
$$RCONH_2 \xrightarrow{P_2O_5} RCN$$
; $CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN + H_2O$
Acetamide

Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.

 $\begin{array}{c} RCOOH + NH_{3} \rightarrow RCOONH_{4} \xrightarrow[-H_{2}O]{} RCONH_{2} \xrightarrow[-H_{2}O]{} RCONH_{2} \xrightarrow[-H_{2}O]{} RCN_{\text{Alkyl cyanide}} \end{array}$

(c) From Grignard reagent

$$\begin{array}{ccc} RMgX + ClCN \rightarrow RCN + Mg \\ & \begin{array}{c} & X \\ Grignard \\ reagent \end{array} & \begin{array}{c} X \\ Cl \\ & \begin{array}{c} Cl \\ Methyl magnesium \\ bromide \end{array} & \begin{array}{c} ClCN \\ Cyanogen \\ Chloride \end{array} & \begin{array}{c} CH_3CN + Mg \\ Methylcyanide \end{array} & \begin{array}{c} Br \\ Cl \\ Cl \\ \end{array} \\ \end{array}$$

(d) From primary amines: Primary amines are dehydrogenated at high temperature to form alkyl cyanides. This is also a commercial method.

 $\begin{array}{c} RCH_{2}NH_{2} \xrightarrow{Cu \ or \ Ni} RCN + 2H_{2}; \ CH_{3}CH_{2}NH_{2} \xrightarrow{Cu \ or \ Ni} CH_{3}CN + 2H_{2} \\ \xrightarrow{Ethylamine} S00^{\circ}C \xrightarrow{Cu \ or \ Ni} CH_{3}CN + 2H_{2} \end{array}$

(e) From oximes:
$$R - \overset{I}{\underset{Aldoxime}{C}} = NOH \xrightarrow{P_2O_5} R - CN + H_2O$$

(ii) Physical properties

(a) Alkyl cyanides are neutral substance with pleasant odour, similar to bitter almonds.

(b) Lower members containing up to 15 carbon atoms are liquids, while higher members are solids.

(c) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

- (d) They are soluble in organic solvents.
- (e) They are poisonous but less poisonous than HCN

(iii) Chemical properties

(a) Hydrolysis

$$\begin{array}{c}
RCN & \xrightarrow{H_2O} RCONH_2 \xrightarrow{H_2O} RCOOH + NH_3 \\
\text{Amide} & \xrightarrow{H_2O} H^+ RCOOH + NH_3 \\
CH_3 CN & \xrightarrow{H_2O} H^+ CH_3 CONH_2 \xrightarrow{H_2O} H^+ CH_3 COOH + NH_3 \\
\text{Methyl} & \xrightarrow{H^+} CH_3 CONH_2 \xrightarrow{H^+} H^+ RCOOH + NH_3 \\
\end{array}$$

(b) Reduction: When reduced with hydrogen in presence of Pt or Ni, or LiAlH₄ (Lithium aluminum hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

$$\begin{array}{c} RCN \\ Alkyl cyanide \end{array} \xrightarrow{4H} RCH_2 NH_2 \\ Primary amine \end{array}$$

However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (Stephen's reaction).

$$R - C \equiv N \xrightarrow{SnCl_2/HCl} RCH = NH.HCl \xrightarrow{H_2O} RCHO + NH_4Cl$$

[2H] Imine hydrochlor ide

(c) Reaction with Grignard reagent: With grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.

(d) Alcoholysis:
$$\underset{\substack{Alkyl\\cyanide}}{RCN} + \frac{R'OH}{H} + HCl \rightarrow \begin{bmatrix} & & \\ & NH_2 \\ & & \\ R - C - OR' \end{bmatrix} Cl^- \xrightarrow{H_2O} RCOOR' + NH_4Cl$$
imido ester

(iv) Uses: Alkyl cyanides are important intermediates in the laboratory synthesis of a large number of compounds like acids, amides, esters, amines etc.

(2) Alkyl Isocyanides

(i) Methods of preparation

(a) From alkyl halides: $R - X_{Alkyl halide} + AgCN \rightarrow RNC_{Isocyanide} + RCN_{Cyanide} (Nitrile) Main product + RCN_{Cyanide} (Nitrile) Minor product + AgCN \rightarrow CH_3NC_{Methyl isocyanide} + CH_3CN_{Methyl isocyanide} +$

(b) From primary amines (Carbylamine reaction) : $RNH_2 + CHCl_3 + 3KOH \rightarrow RNC_{Isocyanide} + 3KCl + 3H_2O$ Primary amine Chloroform

(c) From N-alkyl formamides:
$$R - NH - C - H \xrightarrow{POCl_3} R - N_{Isocyanide} C + \mathbb{Z}_2O$$

(ii) Physical properties

(a) Alkyl isocyanides are colourless, unpleasant smelling liquids.

(b) They are insoluble in water but freely soluble in organic solvents.

(c) Isonitriles are much more poisonous than isomeric cyanides.

(iii) Chemical properties

- (a) Hydrolysis: $RN \stackrel{=}{=} C + 2H_2O \xrightarrow{H^+} RNH_2 + HCOOH_{\text{Primary amine}} HCOOH_{\text{Formic acid}}$
- (b) Reduction: $R N \stackrel{=}{=} C + 4H \xrightarrow{Ni} RNHCH_{3}$ Alkylisocyanide

(c) Action of heat: When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.

 $RNC \xrightarrow{\text{heat}} RCN$

(d) Addition reaction: Alkyl isocyanide give addition reactions due to presence of unshared electron pair on carbon atom.

$$R: N ::: C : \text{or } R - N \equiv C$$

The following are some of the addition reactions shown by alkyl iscoyanides.

 $RNC + X_{2} \rightarrow RNCX_{2} ; RNC + S \rightarrow RNCS_{Alkyl} ; RNC + HgO \rightarrow RNCO + HgO_{Alkyl} ; RNC + HgO \rightarrow RNCO + HgO_{Alkyl} ; isothiocya nate ; RNC + HgO \rightarrow RNCO + HgO_{Alkyl} ; isothiocya nate ; RNC + HgO \rightarrow RNCO + HgO_{Alkyl} ; isothiocya nate ; RNC + HgO_{Alkyl} ; is$

(iv) Uses: Due to their unpleasant smell, alkyl isocyanides are used in detection of very minute leakage. Carbylamine reaction is used as a test for the detection of primary amino group.

Note: Methyl isocyanate (MIC) gas was responsible for Bhopal gas tragedy in Dec. 1984.

□ Cyanides have more polar character than isocyanides. Hence cyanides have high b.p., and are more soluble in water. However, both isomers are more polar than alkylhalides, hence their boiling points are higher than the corresponding alkyl halides.

□ Being less polar, isocyanides are not attacked by OH⁻ ions.

Comparison of Alkyl Cyanides and Alkyl Isocyanides

Test	Ethyl cyanide	Ethyl isocyanide
Smell	Strong but pleasant	Extremely unpleasant
Dipole moment	More (≈ 4D)	Less (≈ 3D)
B.P.	98°C(i.e. High)	78°C (i.e. low)
Solubility in water.	Soluble	Only slightly soluble
Hydrolysis with acids	Gives propionic acid (Acid, in general)	Give ethyl amine (1° amine, in general)
Hydrolysis with alkalies	Same as above	No action
Reduction	Gives propylamine (1° amine, in general)	Gives ethylmethyl amine (2° amine, in general)
Stephen's reaction	Gives propionaldehyde (Aldehyde, in general)	Does not occur
Heating (250°C)	No effect	Ethyl cyanide is formed