

Cyanides and Isocyanides

Hydrogen cyanide is known to exist as a tautomeric mixture.



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



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
CH ₃ CN	Methyl cyanide(Acetonitrile)	Ethane nitrile
C ₂ H ₅ CN	Ethyl cyanide(Propionitrile)	Propane nitrile
C ₃ H ₇ CN	Propyl cyanide	Butane nitrile
C ₄ H ₉ CN	Butyl cyanide	Pentane nitrile

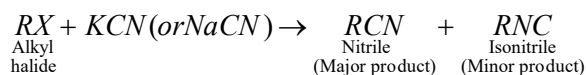
Iso cyanides are named as "Alkyl carbylamine" or "Carbyl amino alkane".

Formula	As isocyanide(Comman name)	IUPAC name
CH ₃ NC	Methyl isocyanide (Methyl isonitrile)	Methyl carbylamine (Carbylamino methane)
C ₂ H ₅ NC	Ethyl isocyanide (Ethyl isonitrile)	Ethyl carbylamine (Carbylamino ethane)
C ₃ H ₇ NC	Propyl isocyanide (Propyl isonitrile)	Propyl carbylamine (Carbylamino propane)

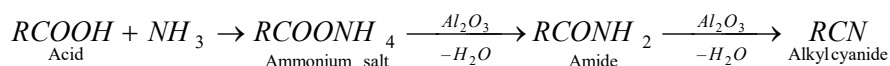
(1) Alkyl Cyanides

(i) Methods of preparation

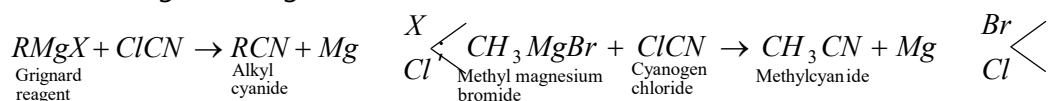
(a) From alkyl halides: The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.



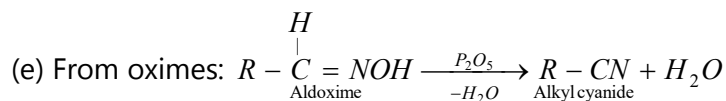
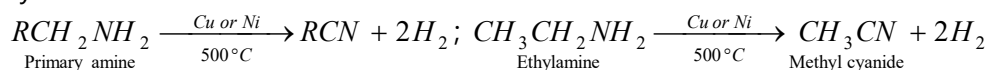
Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at 500°C.



(c) From Grignard reagent



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



(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.

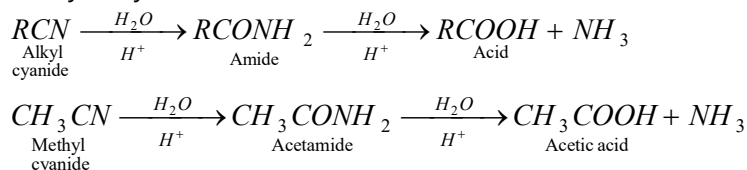
(c) They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule.

(d) They are soluble in organic solvents.

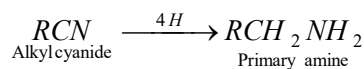
(e) They are poisonous but less poisonous than HCN

(iii) Chemical properties

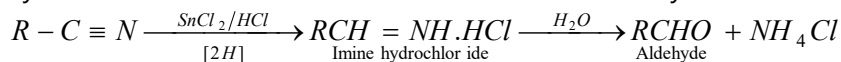
(a) Hydrolysis



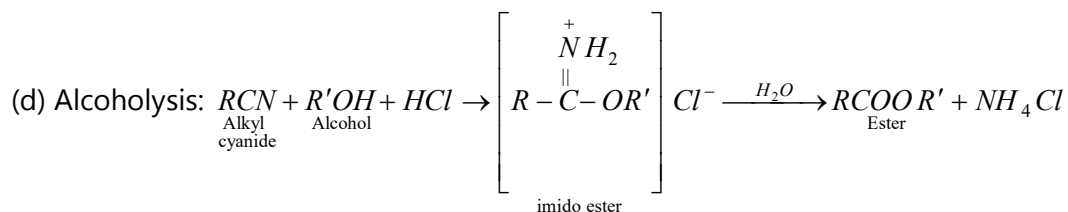
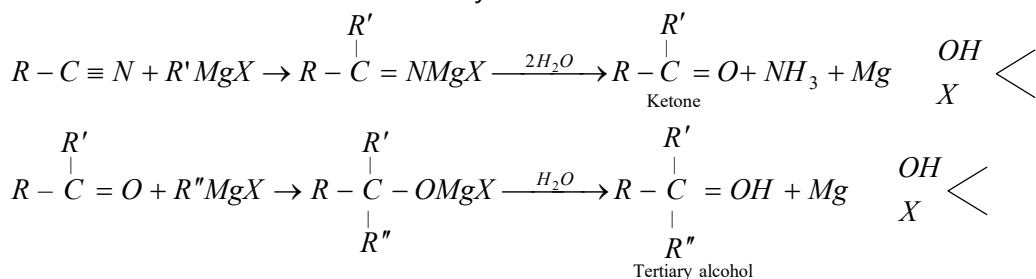
(b) Reduction: When reduced with hydrogen in presence of Pt or Ni, or LiAlH₄ (Lithium aluminum hydride) or sodium and alcohol, alkyl cyanides yield primary amines.



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).



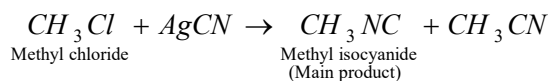
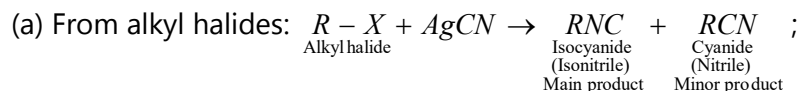
(c) Reaction with Grignard reagent: With grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.



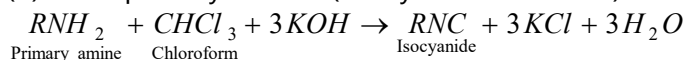
(iv) Uses: Alkyl cyanides are important intermediates in the laboratory synthesis of a large number of compounds like acids, amides, esters, amines etc.

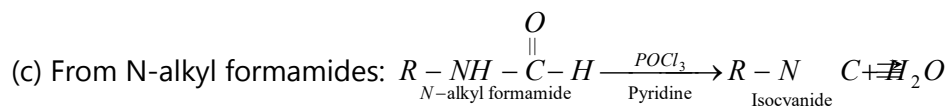
(2) Alkyl Isocyanides

(i) Methods of preparation



(b) From primary amines (Carbylamine reaction) :





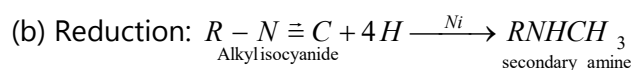
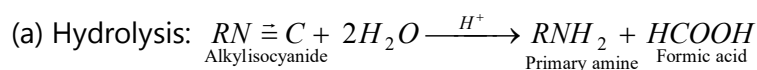
(ii) Physical properties

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

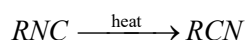
(b) They are insoluble in water but freely soluble in organic solvents.

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

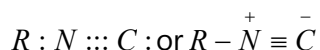
(iii) Chemical properties



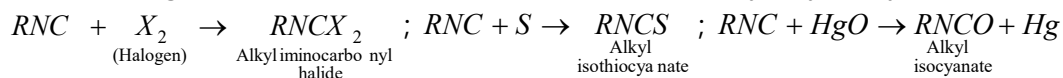
(c) Action of heat: When heated for sometime at 250°C, a small amount of isonitrile changes into isomeric nitrile.



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



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



(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 ($\approx 4D$)	Less ($\approx 3D$)
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