Alkyl nitrites and nitro alkanes.

Nitrous acid exists in two tautomeric forms.

Corresponding to these two forms, nitrous acid gives two types of derivatives, i.e., alkyl nitrites and nitro alkanes.

$$R - O - N_{\text{Alkyl nitrite}} = O; R - N O_{\text{Nitro alkane}}$$

It is important to note that nitro alkanes are better regarded as nitro derivatives of alkanes, while alkyl nitrites are regarded as alkyl esters of nitrous acid.

(1) Alkyl nitrites : The most important alkyl nitrite is ethyl nitrite. Ethyl nitrite (C_2H_5ONO)

(i) General methods of preparation : It is prepared

(a) By adding concentrated HCl or H_2SO_4 to aqueous solution of sodium nitrite and ethyl alcohol at very low temperature (0°C).

NaNO ₂ + HCl \rightarrow NaCl + HNO ₂

$$C_2H_5OH + HNO_2 \rightarrow C_2H_5ONO + H_2O$$

Ethyl nitrite

(b) From Ethyl iodide $C_2H_5I + KONO \rightarrow C_2H_5ONO + KI$ Ethyl iodide

(c) By the action N_2O_3 on ethyl alcohol.

$$2C_2H_5OH + N_2O_3 \rightarrow 2C_2H_5ONO + H_2O$$

(ii) Physical properties

(a) At ordinary temperature it is a gas which can be liquified on cooling to a colourless liquid (b.p.17°C) having characteristic smell of apples.

(b) It is insoluble in water but soluble in alcohol and ether.

(iii) Chemical properties

(a) Hydrolysis : It is hydrolysed by aqueous alkalies or acids into ethyl alcohol. $C_2H_5ONO + H_2O \xrightarrow{NaOH} C_2H_5OH + HNO_2$

(b) Reduction : $C_2H_5ONO + 6H \xrightarrow{Sn} C_2H_5OH + NH_3 + H_2O$

Small amount of hydroxylamine is also formed. $C_2H_5ONO + 4H \rightarrow C_2H_5OH + NH_2OH$

(iv) Uses

(a) Ethyl nitrite dialates the blood vessels and thus accelerates pulse rate and lowers blood pressure, so it is used as a medicine for the treatment of asthma and heart diseases (angina pectoris).

(b) Its 4% alcoholic solution (known as sweet spirit of nitre) is used in medicine as a diuretic.

(c) Since it is easily hydrolysed to form nitrous acids, it is used as a source of nitrous acid in organic synthesis.

Note: Isoamyl nitrite is used as an antispasmodic in angina pectoris and as a restorative in cardiac failure.

(2) Nitro alkanes or Nitroparaffins : Nitro alkanes are regarded as nitro derivatives of hydrocarbons.

(i) Classification : They are classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro groups is linked.

$$\begin{array}{c} RCH_2NO_2 \\ Primary nitro alkane \end{array}; \begin{array}{c} R \\ R \\ R \\ Secondary nitro alkane \end{array}; \begin{array}{c} R \\ R \\ R \end{array} \begin{array}{c} C-NO_2 \\ C-NO_2 \\ R \end{array}$$

(ii) General methods of preparation

(a) By heating an alkyl halide with aqueous alcoholic solution of silver nitrite

 $C_2H_5Br + AgNO_2 \rightarrow C_2H_5NO_2 + AgBr$

Some quantity of alkyl nitrite is also formed in this reaction. It can be removed by fractional distillation since alkyl nitrites have much lower boiling points as compared to nitro alkanes.

(b) By the direct nitration of paraffins (Vapour phase nitration)

 $CH_3CH_3 + HONO_2$ (fuming) $\xrightarrow{400^{\circ}C} CH_3CH_2NO_2 + H_2O$

With higher alkanes, a mixture of different nitro alkanes is formed which can be separated by fractional distillation.

(c) By the action of sodium nitrite on α -halo carboxylic acids

 $\begin{array}{c} CH_{2}ClOOH & \xrightarrow{NaNO_{2}} CH_{2}NO_{2}COOH & \xrightarrow{\text{heat}} CH_{3}NO_{2} + CO_{2} \\ \alpha - \text{Chloro acetic acid} & \xrightarrow{Nitro methane} \end{array}$

(d) By the hydrolysis of α -nitro alkene with water or acid or alkali (Recent method)

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{L} CH_$$

(e) Tertiary nitro alkanes are obtained by the oxidation of t-alkyl amines with KMnO₄. $R_3CNH_2 \xrightarrow{KMnO_4} R_3CNO_2 + H_2O$

(iii) Physical properties

(a) Nitro alkanes are colourless, pleasant smelling liquids.

(b) These are sparingly soluble in water but readily soluble in organic solvents.

(c) Their boiling points are much higher than isomeric alkyl nitrites due to polar nature.

(d) Again due to polar nature, nitro alkanes are excellent solvents for polar and ionic compounds.

Note: 1° and 2° - Nitro alkanes are known to exist as tautomeric mixture of nitro-form and aci-form.

$$\begin{array}{ccc} CH_{3}-N=O & CH_{2}=N-OH \\ & & & \\ O & & & \\ (nitro-form) & (aci-form) \end{array}$$

(iv) Chemical properties

(a) Reduction : Nitro alkanes are reduced to corresponding primary amines with Sn and HCl or Fe and HCl or catalytic hydrogenation using nickel as catalyst.

 $RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$

However, when reduced with a neutral reducing agent (Zinc dust + NH₄Cl), nitro alkanes form substituted hydroxylamines.

 $R - NO_2 + 4H \xrightarrow{Zn+NH_4Cl} R - NHOH + H_2O$

(b) Hydrolysis: Primary nitro alkanes on hydrolysis form hydroxylamine and carboxylic acid. $RCH_2NO_2 + H_2O \xrightarrow{HCl \text{ or } 80\%H_2SO_4} RCOOH + NH_2OH$

secondary nitro alkanes on hydrolysis form ketones.

$$2R_2CHNO_2 \xrightarrow{HCl} 2R_2CO + N_2O + H_2O$$
_{Ketone}

(c) Action of nitrous acid: Nitrous acid reacts with primary, secondary and tertiary nitro alkanes differently.

$$\begin{array}{cccc} R - \underset{NO_2}{CH_2} + \underset{Nitrous acid}{O} = NOH & \xrightarrow{-H_2O} R - \underset{I}{C} = NOH & \xrightarrow{NaOH} R - \underset{I}{C} = NONa \\ & & & & & & \\ NO_2 & & & & & \\ Primary & & & & \\ NO_2 & & & & \\ R_2 & CH + HON = O & \xrightarrow{-H_2O} R_2 & C - NO & \xrightarrow{\text{Ether or}} \\ & & & & & \\ NO_2 & & & & \\ NO_2 & & & & \\ Seconary & & & & \\ Pseudo nitrol \end{array}$$

Tertiary nitro alkanes do not react with nitrous acid.

(d) Thermal decomposition: $R.CH_2.CH_2NO_2 \xrightarrow{>300\,^{\circ}C} R.CH = CH_2 + HNO_2$

On rapid heating nitro alkanes decompose with great violence.

$$CH_3 NO_2 \xrightarrow{\text{heat, Rapidly}} \frac{1}{2}N_2 + CO_2 + \frac{3}{2}H_2$$

(e) Halogenation: Primary and secondary nitro alkanes are readily halogentated in the α -position by treatment with chlorine or bromine.

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$$CH_{3} - NO_{2} \xrightarrow{Cl_{2}} NO_{2} \xrightarrow{Cl_{2}} NO_{2} \xrightarrow{Cl_{3}} NO_{2} \xrightarrow{Cl_{3} + NO_{2}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{Cl_{2} + NaOH} CH_{3} \xrightarrow{CH_{3}} CH_{3} CH_{3} \xrightarrow{CH_{3}} CH_{3} CH_{3} CH_{3} \xrightarrow{CH_{3}} CH_{3} CH_{3} CH_{3} CH_{3$$

(f) Condensation with aldehyde: $CH_3CHO + CH_3NO_2 \rightarrow CH_3CH(OH)CH_2NO_2$ β -Hydroxy nitropropa ne (nitro alcohol)

(g) Reaction with grignardreagent: The aci-form of nitroalkane reacts with Grignard reagent forming alkane.

$$RCH = N \qquad \underset{O}{\overset{OH}{\longrightarrow}} + CH_{3}MgI \rightarrow \underset{Methane}{CH_{4}} + RCH = N \qquad \underset{O}{\overset{OMgI}{\longrightarrow}}$$

Note: The nitrogen of $-NO_2$ carrying a positive charge exerts a powerful – I effect and thus activates the hydrogen atom of the α -carbon. Thus the important reactions of nitroalkanes are those which involve α -hydrogen atom of primary and secondary nitroalkanes (tertiary nitroalkanes have no α -hydrogen atom and hence do not undergo such type of reactions).

 \Box Acidic character: The α -hydrogen atom of primary and secondary nitroalkanes are weakly acidic and thus can be abstracted by strong alkalies like aq. NaOH. Therefore, 1° and 2° nitroalkanes dissolve in aq. NaOH to form salts. For examples.

$$CH_{3} - \overset{+}{N} \quad \overset{O}{O_{-}} \underbrace{\overset{NaOH}{\longrightarrow} O}_{I} \underbrace{\overset{-}{\nabla} A^{+} \overset{-}{C} H_{2} - \overset{+}{N}}_{I} \quad \overset{O}{O} \leftrightarrow H_{2}C = \underbrace{\overset{+}{\nabla} O \overset{-}{N} a}_{O_{-}} \quad <$$

Thus 1° and 2° nitroalkanes are acidic mainly due to following two reasons, (a) Strong electron withdrawing effect of the $- NO_2$ group.

(b) Resonance stabilisation of the carbanion (I) formed after the removal of proton. The aci-form of nitroalkanes is relatively more acidic because it produces relatively more conjugate base.

- (v) Uses: Nitro alkanes are used,
- (a) As solvents for polar substances such as cellulose acetate, synthetic rubber etc.
- (b) As an explosive.
- (c) For the preparation of amines, hydroxylamines, chloropicrin etc.

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Test	Ethyl nitrite (C₂H₅ONO) (Alkyl nitrite, RONO)	Nitro ethane ($C_2H_5NO_2$) (Nitro alkane, RNO ₂)
Boiling point	Low, 17°C	Much higher, 115°C
Reduction with metal and acid (Sn/HCl) or with LiAlH ₄ .	Gives alcohol + hydroxyl amine or NH ₃ . $C_2H_5ONO + 4H \rightarrow C_2H_5OH + NH_2OH$ $RONO + 6H \rightarrow ROH + NH_3 + H_2O$	Gives corresponding primary amine. $C_2H_5NO_2 + 6H \rightarrow C_2H_5NH_2 + 2H_2O$ $RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$
Action of NaOH (alkalies).	Readily hydrolysed to give corresponding alcohol and sodium nitrite (decomposition). $C_2H_5ONO + NaOH \rightarrow C_2H_5OH + NaNO_2$ $RONO + NaOH \rightarrow ROH + NaNO_2$	Not decomposed, i.e., alcohols are not produced. But it may form soluble sodium salt, because in presence of alkali the nitro form changes into aci form, which dissolves in alkalies to form sodium salt. $CH_3 - CH = N \xrightarrow{OH}_{O} \xrightarrow{NaOH}_{O} - CH_3 - CH = N \xrightarrow{ONa}_{O}$
Action of HNO ₂ (NaNO ₂ + HCl)	No action with nitrous acid.	Primary nitro alkanes forms nitrolic acid, which dissolve in alkali to give red solution. Secondary nitro alkane yields pseudo-nitrol, which dissolves in alkali to give blue solution.

Distinction between Ethyl nitrite and Nitro ethane