Alkanes -2: Chemical Reactions

Kumud Bala

The reactivity of various hydrocarbons is directly related to their structures. Alkanes are saturated hydrocarbons. These contain only C-C and C-H sigma bonds. Since these bonds are quite strong, alkanes are the least reactive of all the hydrocarbons. It is because of this relative inertness that alkanes are called paraffins (latin: parum = little, affinis = affinity or reactivity). Some important chemical reactions of alkanes are:

(1) Substitution reactions: A reaction in which a hydrogen atom of a hydrocarbon is replaced by an atom or a group of atoms is called a substitution reaction. Alkanes, because of having only C- C Bond and C-H sigma bonds undergo only substitution reaction. For example,

(i) Halogenation of alkanes: halogenations of an alkane are carried out by treating it with a suitable halogen in presence of ultraviolet light or by heating the reaction mixture to 520 -670 K. The order of reactivity of different halogens in this reaction is: $F_2 > Cl_2 > Br_2 > I_2$

Chlorination: During chlorination of methane, all the four hydrogen atoms are replaced one by one to form a mixture of products. for example,

$$\underset{\text{methane}}{CH_4} + Cl_2 \xrightarrow{hv \text{ or } 520\text{-}670K} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$\underset{\text{Chloromethane}}{CH_3Cl} + Cl_2 \xrightarrow{hv} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$\underset{\text{Dichloromethane}}{CH_2Cl_2} + Cl_2 \xrightarrow{hv \text{ or } 520\text{-}670K} \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$\underset{\text{Trichloromethane}}{CHCl_3} + Cl_2 \xrightarrow{hv \text{ or } 520\text{-}670K} \underset{\text{Tetra chloromethane}}{CCl_4} + HCl$$

Bromination: bromine reacts with alkanes in a similar manner but less readily.

$$CH_3\text{-}CH_3 + Br_2 \xrightarrow{hv \text{ or } 520\text{-}670K} \underset{\text{Bromoethane}}{CH_3\text{-}CH_2\text{-}Br} + HBr$$

Iodination: The reaction of iodine with alkane is reversible because the hydrogen iodide formed as a by-product is a moderate reducing agent and hence reduces the iodoalkane back to alkane.

$$CH_4 + I_2 \leftrightarrow \underset{\text{Iodomethane}}{CH_3I} + HI$$

Thus, direct iodination of alkane cannot be brought about. However, the iodination can be carried out in presence of anoxidizing agent such as iodic acid (HIO_3), nitric acid (HNO_3) or mercuric oxide (HgO) which converts HI to I_2 as it is formed:

$$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$

$$2HNO_3 + 2HI \rightarrow 2H_2O + 2NO_2 + I_2$$

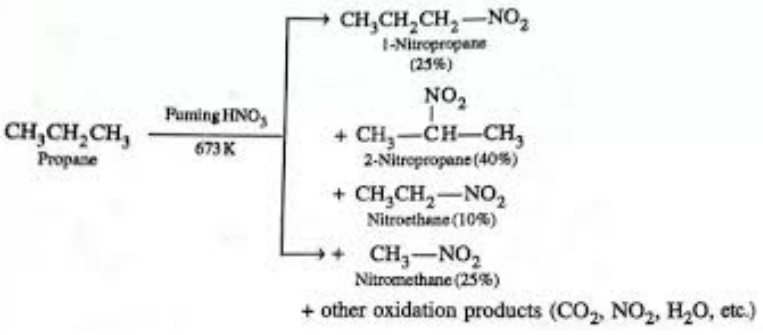
$$HgO + 2HI \rightarrow HgI_2 + H_2O$$

Fluorination: fluorination of alkanes is too vigorous to be controlled under ordinary conditions. Furthermore, fluorination brings about extensive rupture of C-C and C-H bonds leading to a mixture of products. Thus, fluorination of alkanes with pure fluorine is of little practical use. However, fluorination of alkanes can be carried out by diluting fluorine with an inert gas such as nitrogen or argon. Alternatively, alkyl fluorides are more conveniently prepared indirectly by heating suitable chloro alkanes with inorganic fluorides such as AsF_3 , SbF_3, AgF, Hg_2F_2, etc. For example,

$$2CH_3\text{-}CH_2\text{-}Cl + Hg_2F_2 \rightarrow 2CH_3CH_2\text{-}F + Hg_2Cl_2$$

This reaction is called Swart's reaction.

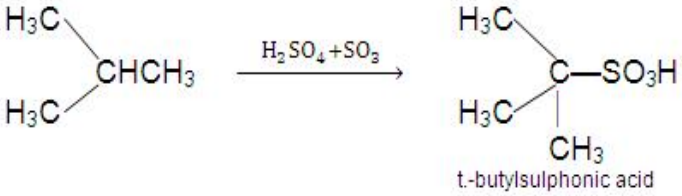
(ii) Nitration: The process of replacement of a hydrogen atom by a nitro ($-NO_2$) group is called nitration. At ordinary temperatures, alkanes do not react with nitric acid. However, when a mixture of an alkane and fuming nitric acid vapour are heated at 423 – 673K under pressure (vapour phase nitration), alkanes undergo nitration giving a mixture of nitroalkanes resulting through cleavage of carbon - carbon bonds. For example,



CH_3-H + HNO_3 $\rightarrow$ CH_3-NO_2 + H_2O

The order of reactivity of different hydrogens in this reaction is 3°> 2° >1° .

(iii) Sulphonation: Substitution of a hydrogen atom of an alkane by sulphonic acid group ($-SO_3H$) is called sulphonation. It is carried out by heating alkane with fuming sulphuric acid ($H_2SO_4 + SO_3$) at 675- 775 K. Branched chain and higher normal alkanes (containing six or more carbon atoms) undergo sulphonation to give alkanesulphonic acids. The ease of substitution of hydrogen is 3° > 2° > 1°.



$CH_3(CH_2)_4CH_3$ + H_2SO_4 $\rightarrow^{SO3,\ 675K}$ $CH_3(CH_2)_4CH_2$- SO_3H + H_2O

n-Hexane n-Hexanesulphonic acid

(2) Oxidation: some important oxidation reactions of alkanes are:

(a) Complete oxidation or combustion: on heating, alkane readily burn in air or oxygen producing CO_2 and H_2O. This process is called combustion.

CH_4 (g) + $2O_2$ (g) $\rightarrow$ CO_2 (g) + $2H_2O$ (l) $\Delta_cH° = -890 kJmol^{-1}$

C_4H_{10} (g) + 13/2 O_2 $\rightarrow$ $4CO_2$ (g) + $5H_2O$ (l) $\Delta_cH° = -2875.84\ kJmol^{-1}$

The general combustion equation for any alkane is:

C_nH_{2n+2} + $(\frac{3n+1}{2})$ O_2 $\rightarrow$ nCO_2 + (n+1) H_2O.

Since the process of combustion is accompanied by liberation of large amount of heat, therefore, alkanes which are the constituents of LPG (butane and isobutene), gasoline, kerosene oil and diesel are widely used as fuels.

(b) Incomplete combustion: if the combustion of alkanes is carried out in limited supply of air or oxygen, carbon monoxide is produced along with unburnt carbon in the form of carbon black or soot.

$CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$

$CH_4 + O_2 \rightarrow C + H_2O$

Carbon black is used in the preparation of black ink, paints and polishes etc.

Reaction with steam: Methane reacts with steam at 1273K in presence of nickel as catalyst forming carbon monoxide and hydrogen.

$CH_4 + H_2O \rightarrow^{1273K,\ Ni} CO + 3H_2$

This method is used for industrial preparation of dihydrogen.

(c) Catalytic oxidation: different products are formed under different conditions.

(i) When a mixture of Methane and oxygen (9:1 by volume) at a pressure of 100 atm. is passed through a copper tube at 573K, methanol is formed.

$$2CH_4 + O_2 \rightarrow^{100\ atm.\ 573K\ cu\ tube} 2CH_3OH$$

(ii) when a mixture of Methane and oxygen under pressure is passed over heated molybdenum oxide, it is oxidized to methanal.

$$CH_4 + O_2 \xrightarrow{Mo2O3\ \Delta} HCHO + H_2O.$$

(iii) Higher alkanes on oxidation in presence of silver oxide give a carboxylic acid.

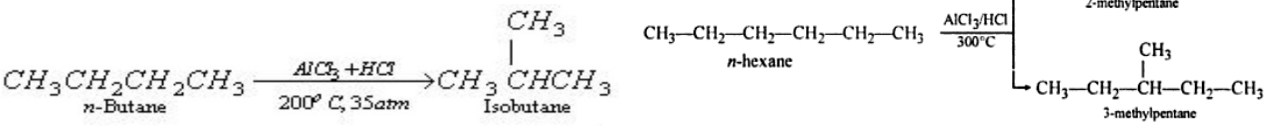
$$2R\text{-}CH_3 + 3O_2 \xrightarrow{Ag2O\ \Delta} 2RCOOH + 2H_2O\ .$$

(iv) In general oxidizing agents such as $KMnO_4$, $K_2Cr_2O_7$ etc. have no effect on alkanes. However, alkane containing tertiary hydrogen can be oxidized to corresponding alcohols.

$$CH_3CH(CH_3)_2 + O \xrightarrow{KMnO4} CH_3C(OH)(CH_3)_2$$

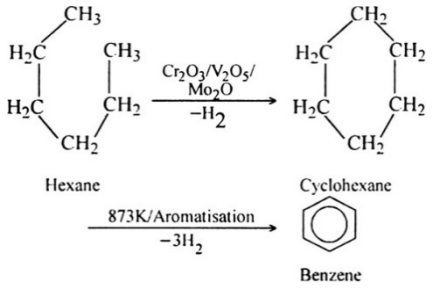
2-methylpropane → 2-methylpropan-2-ol

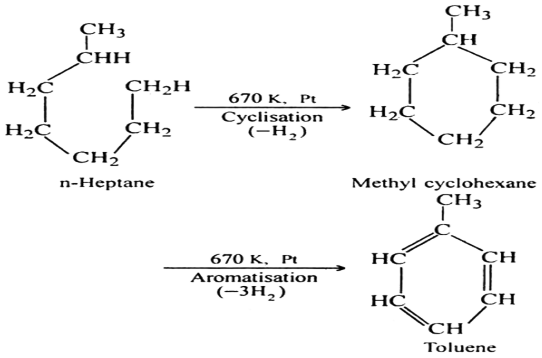
(3) Isomerization: When n-alkanes are heated with anhydrous aluminium chloride and hydrogen chloride at 573 K under a pressure of about 35 atmospheres, they are converted into branched chain alkanes. For example,



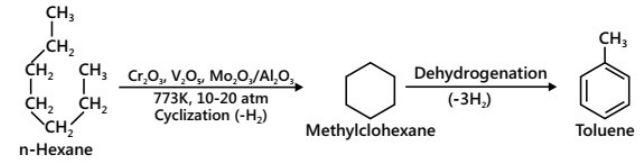
The process of isomerization has been of great utility for increasing the Octane number of a particular petroleum fraction.

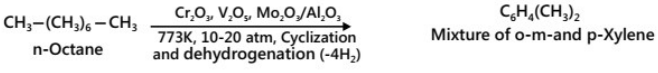
(4) Aromatization: Alkanes containing 6 to8 carbon atoms when heated to about 773K under 10-20 atm. pressure in the presence of a catalyst consisting of oxides of chromium, vanadium and molybdenum supported over alumina get converted into aromatic hydrocarbons. This process which involves cyclization, isomerization and dehydrogenation is called aromatization. For example,

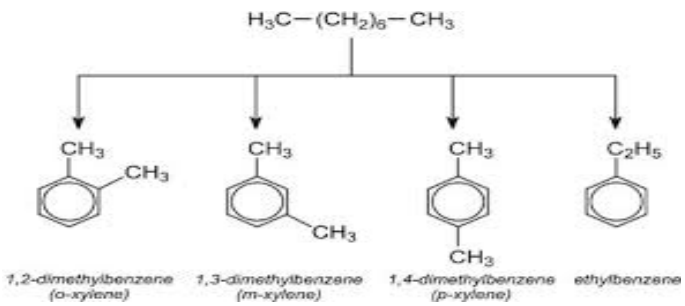




Under similar conditions, n-heptane gives toluene and n-Octane gives mixture of o-, m, p-xylenes.

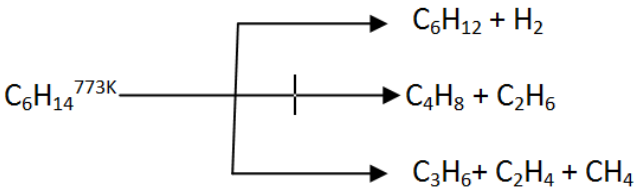


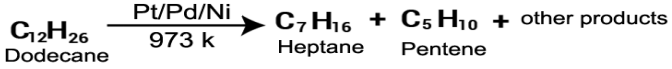




(5) Pyrolysis: Decomposition of a compound by application of heat is called pyrolysis. Pyrolysis of higher alkane into a mixture of alkanes, alkenes, etc. is called tracking. It is usually carried out by heating higher alkanes to High temperatures (773 – 973K) under a pressure of 6-7 atmospheres in the presence or absence of a catalyst. For example,

Pyrolysis of alkanes involves breaking of carbon-carbon and carbon -hydrogen bonds and occurs by a free radical mechanism. Preparation of oil gas from crossing oil and petrol gas from petrol is based upon the process of pyrolysis. For example, dodecane, a constituent of kerosene oil, on heating to





973 Kelvin in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene along with their other products.

Assignment

1. In the alkane, CH_3CH_2-C(CH_3)-CH_2-CH(CH_3)$_2$, identify 1°, 2°, 3° carbon atoms and give the number of H-atoms bonded to 2° carbon atoms.

(A) 15H- atoms attached to 2° carbon
(B) 4H-atoms attached to 2° carbon
(C) 1H-atoms attached to 2° carbon
(D) none of these

2. What will be formed when vapours of hexane are passed over heated catalyst consisting of Cr_2O_3, Mo_2O_3 and V_2O_5 at 773K under 10-20 atm. pressure.

(A) hexane (B) benzene (C) toluene (D) cyclohexane

3. Thermal decomposition of higher hydrocarbons into lower hydrocarbons is called -----

(A) aromatization (B) cracking (C) reforming (D) isomerization

4. Photochemical chlorination is initiated by a process of -----

(A) pyrolysis (B) substitution (C) peroxidation (D) homolysis

5. $CH_3CH_2CH_2CH_3 \rightarrow^{catalyst} CH_3CH(CH_3)_2$. The catalyst used in the above conversion is -------

(A) $ZnCl_2$/HCl (B) $AlCl_3$/HCl (C) $PdCl_2$/HCl (D) CuCl/HCl

6. $CH_3CH_3 + HNO_3 \rightarrow^{675K}$?

(A) $CH_3CH_2NO_2$ (B) $CH_3CH_2NO_2 + CH_3NO_2$ (C) $2CH_3NO_2$ (D) $CH_2=CH_2$

Answers

1. (B) 2. (B) 3. (B) 4. (D) 5. (B) 6. (B)

—00—