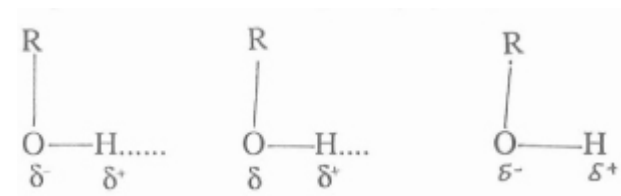


14. ALKANOLS

14.1 Introduction

The replacement of one hydrogen atom in methane, CH_4 , with a hydroxyl, (OH) group yields methanol, CH_3OH . Similarly the replacement of one hydrogen atom in ethane, C_2H_6 by a hydroxyl group yields ethanol, $\text{C}_2\text{H}_5\text{OH}$. Methanol and ethanol are the first and second members of a homologous series known as the alkanols. In general, the alkanols are the products of the replacement of a hydrogen atom in an alkane by a hydroxyl group. They have the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$ or simply ROH where R, the alkyl group is $\text{C}_n\text{H}_{2n+1}$.

The simple alkanols such as methanol, ethanol, or propanol are colourless liquids. They have higher boiling points than alkanes of comparable molar masses because of hydrogen-bonding which exists between their molecules, on account of the polar nature of the hydroxyl group.



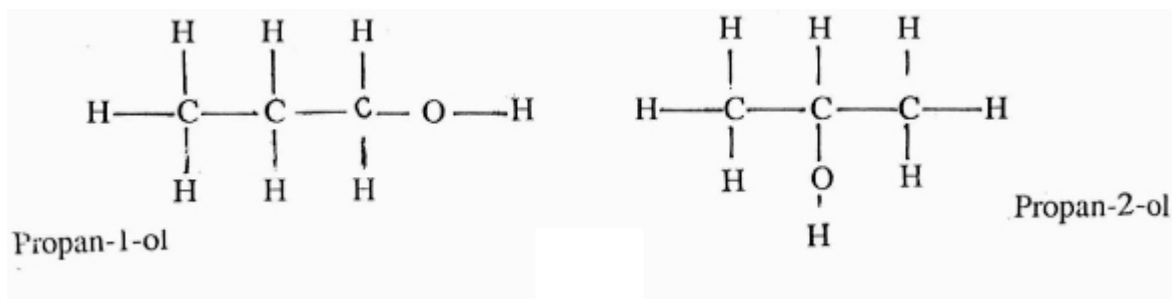
In Table 1, the boiling points of alkanols and alkanes of similar molar mass are compared.

(Table 1)

Alkane	Molar Mass BP($^{\circ}\text{C}$)	
Ethane, C_2H_6	30	-88.6
Propane, C_3H_8	44	-42.2
Butane, C_4H_{10}	58	-0.5
Pentane, C_5H_{12}	72	36
Alkanol		
Methanol, CH_3OH	32	64.5
Ethanol, $\text{C}_2\text{H}_5\text{OH}$	46	78.5
Propanol, $\text{C}_3\text{H}_7\text{OH}$	60	97

14.2 Isomerism in Alkanols

Although propane does not show isomerism, there are two propanol isomers, depending on the position of the hydroxyl group.



In propan-1-ol the hydroxyl group is attached to a terminal carbon atom, whereas in propan-2-ol it is attached to a middle carbon atom.

Exercise (1) Try replacing different hydrogen atoms in butane with a hydroxyl group. How many butanol isomers are possible?

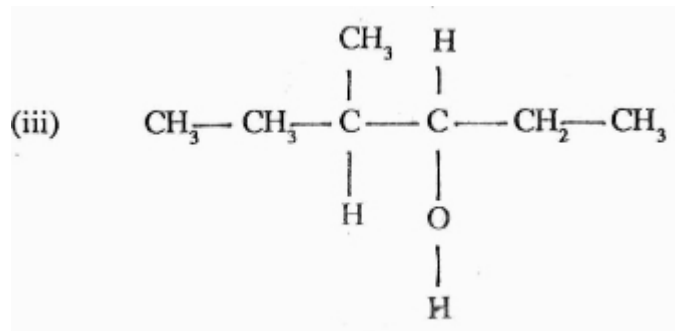
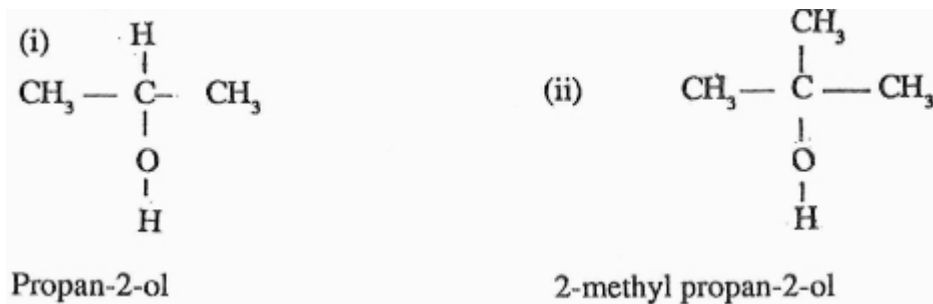
(Note: Do not regard 2-methyl propane as a butane).

Since the position of a hydroxyl group gives rise to isomerism there are theoretically many more isomers for a given molecular formula of an alkanol than for a similar alkane.

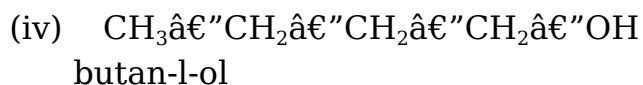
The I.U.P.A.C. system of naming (nomenclature) is used to specify the isomers. The rules to follow in naming the isomers are similar to those for naming the alkanes, viz:

- (i) Select the longest chain of consecutively joined carbon atoms containing the OH group. The alkanol bears the root name of the alkane with that number of carbon atoms.
- (ii) Assign the least possible number to the carbon atom to which the OH group is attached.
- (iii) Indicate other groups present in the molecule and their positions.
- (iv) Change the terminal e in the name of the parent alkane to the suffix *-ol*.

Examples.



4-methyl hexan-3-ol



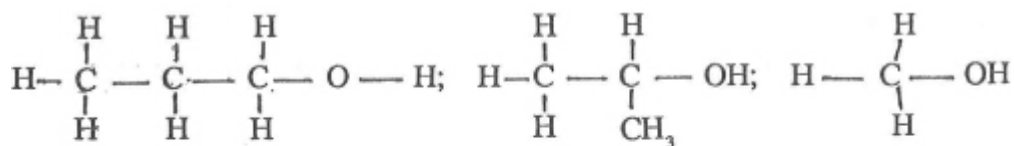
Exercise (2) Name the following alkanols.

- (i) $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$
- (ii) $(\text{CH}_3)_3\text{COH}$
- (iii) $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2$
- (iv) $\text{CO}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CHOH}\text{C}_3$
- (v) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

14.3 Primary, Secondary and Tertiary Alkanols

Alkanols are classified as primary, secondary or tertiary depending on the environment of the hydroxyl group. An alkanol is a primary alkanol if there are two hydrogen atoms (or one alkyl group) on the carbon atom to which the OH group is attached;

(3 hydrogen atoms or no alkyl group on the carbon atom carrying the OH group as in the case of methanol only is also a primary alkanol). If that carbon atom carries only one hydrogen atom (or two alkyl groups) the alkanol is a secondary one, whereas if it carries no hydrogen atom (or three alkyl groups) the alkanol is tertiary.



Propan-1-ol

(i)

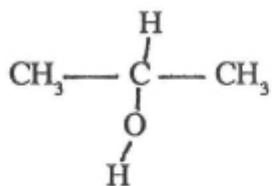
2-methyl propan-1-ol

(ii)

methanol

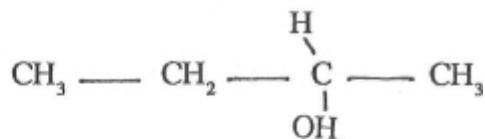
(iii)

(i), (ii), (iii) are Primary alkanols



Propan-2-ol

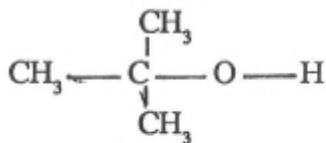
(iv)



butan-2-ol

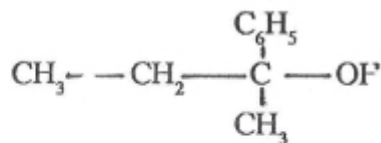
(v)

(iv) & (v) are Secondary alkanols



2-methyl propan-2-ol

(vi)



2-phenyl butan-2-ol

(vii)

(vi) & (vii) are Tertiary alkanols.

Exercise 3. Give one example of a primary, one of a secondary, and one of a tertiary alkanol each with five carbon atoms.

We shall consider some of the reactions of the different classes of alkanols in due course.

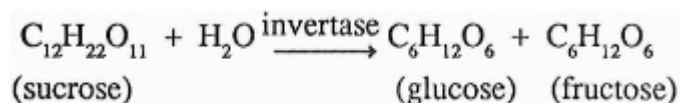
14.3 Preparation of Alkanols

Fermentation

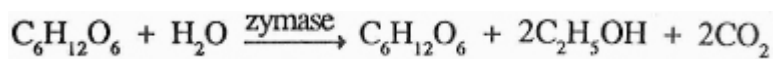
Fermentation is the decomposition of complex organic molecules to simpler ones by the action of enzymes. Ethanol is by far the most widely used alkanol. It is made by the fermentation of carbohydrates followed by distillation. This process was discussed in Book 1, Section 10.8, under the heading "Foods and Beverages".

We can make ethanol in the laboratory from cane sugar. To do this

yeast is added to the cane sugar solution which contains sucrose, and the mixture left for 3-4 days to ferment. During this period an enzyme called *invertase*, present in yeast, catalyses the hydrolysis of sucrose to glucose and fructose.

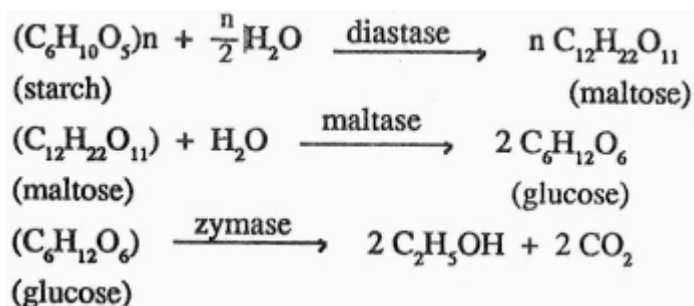


Another enzyme, *zymase*, also present in yeast then catalyses the breakdown of glucose and fructose to ethanol and carbon(IV) oxide.



The frothing observed during the fermentation period is due to the liberation of carbon(IV) oxide. On distilling, a solution of ethanol in water is got as distillate. Redistillation of this initial product eventually yields 95% ethanol and 5% water mixture which has a constant boiling point of 78.Â°C. This alcohol is called **rectified spirit or commercial alcohol**.

Palm wine or cocoa juice, can be used in place of cane sugar. Starchy food materials such as cassava, potatoes, cereals (maize, wheat, rice, guinea com) etc, can also be used as starting materials for fermentation. When they are used the material must first be crushed and steam heated to extract the starch. Malt, partially germinated barley, is then added and the mixture left for about an hour at a temperature of 60Â°C. An enzyme, *diastase*, present in the malt, hydrolyses the starch to maltose. *Maltase*, an enzyme present in yeast, catalyses the conversion of maltose to glucose. *Zymase*, another enzyme present in yeast then catalyses the conversion of glucose to ethanol and carbon(IV) oxide. The ethanol is separated from the other materials in the ferment pot by distillation, after, filtration.



Cellulose-rich materials such as saw dust can also be used as starting material. In this case a mineral acid, hydrogen chloride acid (hydrochloric acid) is used to aid hydrolysis before enzymes are added.

Brewing

The brewing process was also discussed in Book 1, Section 10.8,

Page 213. The reactions involved are exactly the same as those discussed above. Table 10.4, Book 1 (p. 214) is reproduced to show the wide scale use of ethanol as alcoholic beverage.

Table 14.1 Types of Alcoholic Beverages

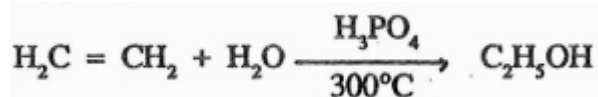
Type	How prepared
Beer (about 5% ethanol)	Fermentation of barley, or cereals. No distillation. Hops added to improve taste and flavour.
Whisky	Prepared by distillation of solution formed after beer is brewed.
Wine	Fermentation of fruit/plant juice. No distillation.
Cognac	Prepared by distillation of fermented grape fruit juice.
Gin	Fermentation of rye or palm wine followed by distillation.
Rum	Distillation of the fermentation product of sugar solution.

Absolute ethanol

Since rectified spirit (95% ethanol), is constant-boiling (eutetic mixture), no amount of distillation can increase its ethanol content. Very pure ethanol (99.5 - 99.9%) can be made from commercial ethanol by treating with quicklime, CaO, keeping overnight, then filtering off the solid and distilling the filtrate. The distillate is collected at 78Å°C.

Large Scale Manufacture of Ethanol

Ethanol is presently manufactured by the hydration of ethene, at 300Å°C, using tetraoxophosphate(V) acid as catalyst.



14.5 Reactions of Alkanols

We expect the alkanols to react alike. Their reactions will be illustrated with methanol and/or ethanol below.

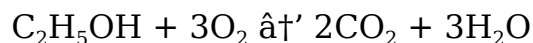
1. Solubility (miscibility) with water

Put about 1 cm³ of methanol or ethanol into a test tube then add about 1 cm³ of water to it and shake. Note that the alkanol and water

are miscible, i.e., the alkanol dissolves in water, or the water dissolves in the alkanol. Hydrogen-bonding between the different molecules is responsible for their miscibility (solubility).

2. Combustion

Put a few drops of methanol or ethanol on a crucible lid and ignite it. Note that the alkanol burns with a blue flame. The products of the combustion are the same as for the combustion of most organic compounds, carbon(IV) oxide and water.



3. Reaction with Sodium

Put about 20cm³ of methanol into a small beaker (50 cm³ capacity). Place a small piece of sodium metal on the surface of the liquid and quickly hold a dry inverted test tube just above the sodium to collect the colourless gas given off. After about 30 seconds bring a lighted taper to the mouth of the test tube now held erect. A pop sound indicates that the gas is hydrogen. Test the resulting liquid in the beaker with red litmus. It turns blue showing that the liquid is now alkaline.

Sodium liberates hydrogen from alkanols, forming an alkaline solution of sodium alkoxide.

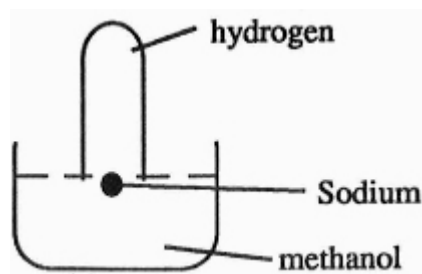
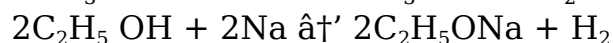
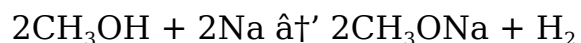


Fig. 14.1



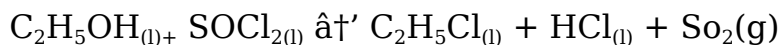
On evaporation to dryness the alkaline solution leaves a white solid, sodium methoxide and sodium ethoxide respectively.

4. Replacement of OH group by a halogen atom

Put about 1 cm³ of absolute, ethanol into a 50 cm³ beaker. Add a little phosphorus(V) chloride to it and test the gas liberated first with wet blue litmus paper, and then with concentrated ammonia solution in a dropper pipette. The blue litmus paper turns red while dense white fumes of ammonium chloride results with the concentrated ammonia solution, showing that the gas liberated is hydrogen chloride. The OH group of the alkanol is replaced with a chlorine atom, producing chloroethane. The equation of the reaction is



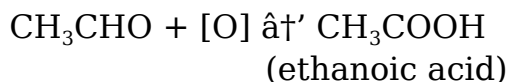
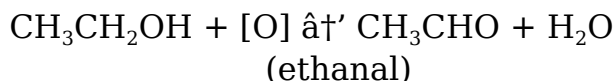
If thionyl chloride, SOCl_2 , is used in place of phosphorus(V) chloride all other products of the reaction except chloroethane, being gaseous will escape. The reaction can be used to prepare chloroethane since separation problems are avoided.



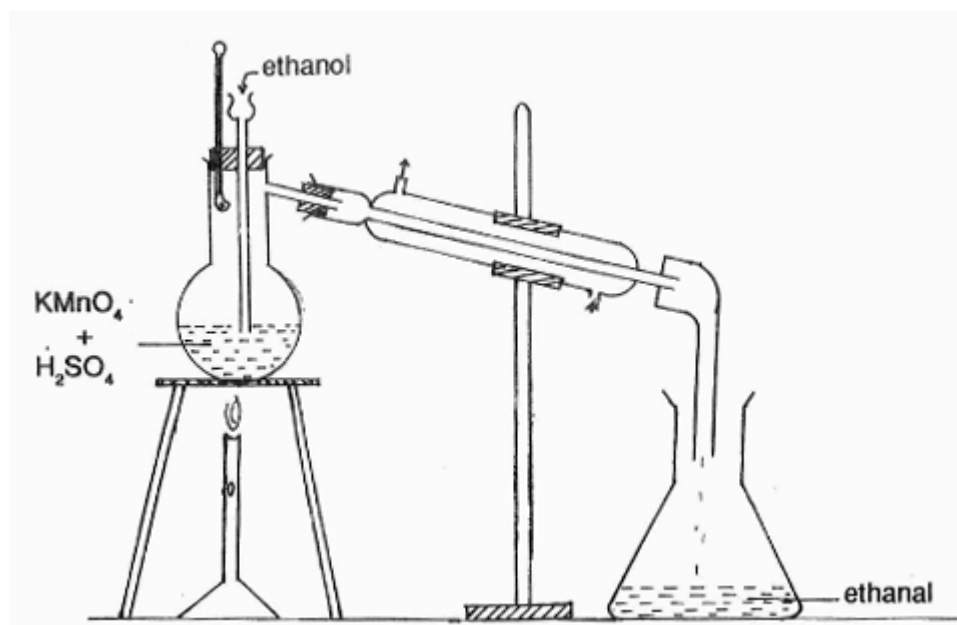
5. Oxidation

Place about 1 cm³ bench potassium tetraoxomanganate(VII) solution into a test tube. Acidify the solution with bench tetraoxosulphate(VI) acid, then add about 2 cm³ of ethanol into the test tube. Shake to mix the reactants and cool the test tube under running tap water. Note the disappearance of the purple colour of potassium tetraoxomanganate(VII) which is evidence that oxidation has taken place. Warm the test tube in a water bath for about 3 minutes for the reaction to go to completion, then note the odour of the product.

Ethanol, a primary alkanol, is oxidized first to ethanal, and then to ethanoic acid.

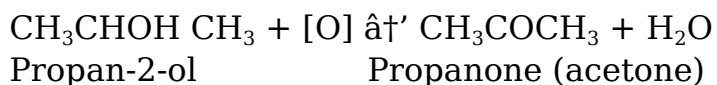


In order to use this reaction to prepare ethanal further oxidation has to be prevented when ethanal has been formed. To achieve this ethanol is added from a dropping funnel into a distillation flask containing the acidified oxidizing agent. Then ethanal distils off as quickly as it is formed and fresh ethanol is added at the rate of distillation. The apparatus is illustrated in Fig. 14.2.



Secondary alkanols are oxidized to alkanones and no further oxidation

is possible, while tertiary alkanols are difficult to oxidize. When they do get oxidized fission of C – C bonds accompany the oxidation.

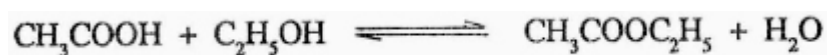


6. Esterification

Put about 1 cm³ of ethanol into a test tube and add one drop of concentrated tetraoxosulphate(VI) acid to it. Next add about 1 cm³ of ethanoic acid to the test tube, then warm in a water bath for about 3 minutes.

Note the odour of the product. The sweet smell of an ester, ethyl ethanoate, indicates that esterification has taken place.

The concentrated tetraoxosulphate(VI) acid acts as a catalyst in the reaction which is reversible.



The preparation of ethyl ethanoate by esterification reaction is discussed fully in Book 3, Experiment 6.3.

7. Dehydration of ethanol

Set up the apparatus shown in Fig. 14.3. Put some asbestos wool soaked in ethanol into the hard glass tube. Add some pieces of broken porous pot, some distance from the asbestos wool and then heat the tube at the position of the porous pot, so strongly that heat is transmitted to the ethanol soaked asbestos wool. Allow some air to escape from the other end and collect the gas liberated over water in a few test tubes.

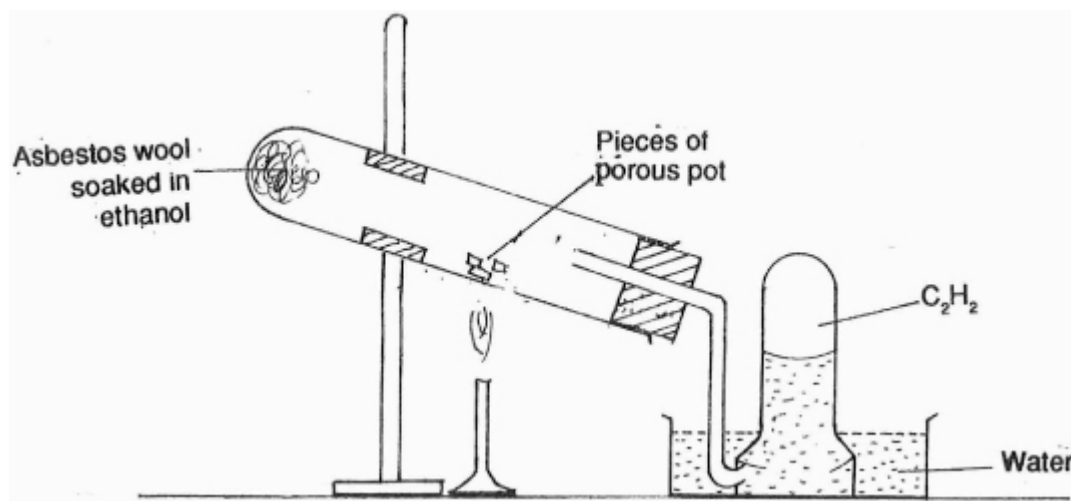
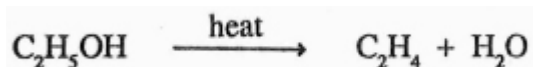


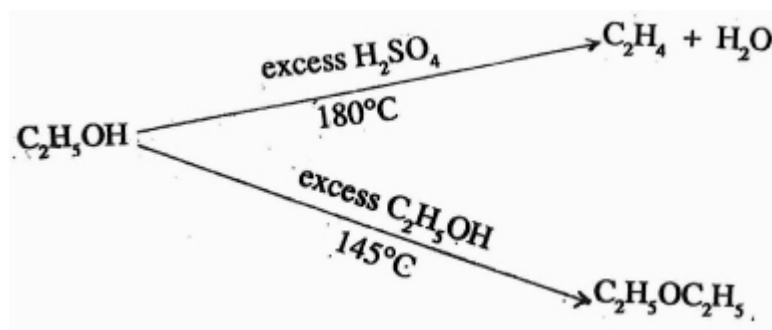
Fig. 14.3 Dehydration of ethanol



Add a few drops of acidified potassium tetraoxomanganate(VII)

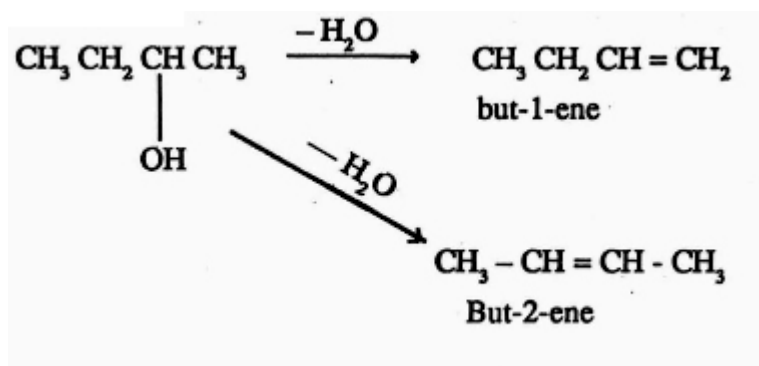
solution into one of the test tubes containing the gas. Note the decolourisation of the purple colour – a test for reducing agent (unsaturation). Bring a lighted taper near the mouth of another test tube of the gas and note that it burns with a luminous flame, again indicating unsaturation. The gas is ethene. It is formed by the dehydration of ethanol.

The dehydration can be effected with concentrated tetraoxosulphate(VI) acid at 180°C . At 145°C , in the presence of excess ethanol, however, ethylethoxide (diethyl ether) forms instead.



(See Preparation of ethene, in Chapter 13 of this Book.

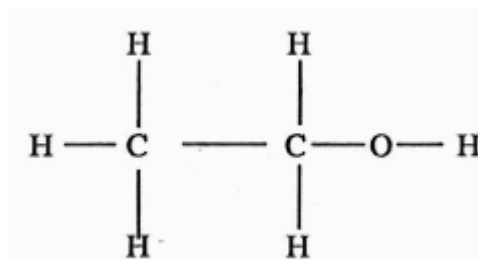
Similar dehydration of butan-2-ol, a secondary alkanol, yields two isomeric products:



14.6 The Structure of ethanol

Experimental analysis shows that ethanol contains 52.2% C, 13.1% H and 34.7% O. Its molecular formula is thus $\text{C}_2\text{H}_6\text{O}$.

The reaction with sodium in which one H atom is replaced by Na suggests that one of the six hydrogen atoms is differently attached. The reaction with phosphorus(V) chloride in which a chlorine atom replaces one oxygen and one hydrogen atom suggests that the differently attached H atom is bonded to oxygen and not directly to carbon. The oxidation products suggest that the two C atoms are linked. To satisfy the combining powers of carbon, oxygen and hydrogen we therefore propose the following as structure for ethanol.



14.7 Polyhydroxyl alkanols

An alkanol with only one OH group in a molecule, such as methanol, ethanol, propan-1-ol, propan-2-ol etc, is described as *monohydric*. Those with two hydroxyl groups per molecule, such as ethane-1-diol, $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$, which is used as an antifreeze agent in automobile cooling systems, are *dihydric*.

Many naturally occurring compounds contain more than two OH groups in one molecule and are described as *polyhydroxyl alkanols*.

Glycerol (propane-1, 2, 3-triol) is a trihydroxyl alkanol. It is a viscous fluid, and a bye product in the manufacture of soap (See Book 3, p. 154). It is used in the manufacture of nitroglycerin, an explosive, and in the formulation of pharmaceuticals. Glucose (see Book 3 p. 171) and the other carbohydrates are polyhydroxyl-alkanols.

14.8 Uses of ethanol

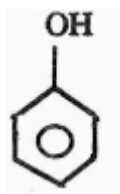
1. The most common use of ethanol is as alcoholic beverage. It is a constituent of many drinks, notably beer, brandy, whisky, gin, rum, cider etc.
2. Ethanol also finds use as a fuel for lighting stoves and as a surgical spirit. Methylated spirit is 5% methanol, 95% ethanol.
3. Ethanol is used extensively as solvent in industry and in research.
4. It is used in the manufacture of many other organic compounds such as ethanal, ethanoic acid, etc.
5. It is used in the manufacture of toiletries eg. perfumes etc.

14.9 Test for alkanols

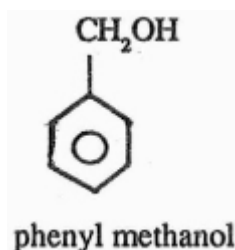
Some of the reactions of alkanols described above can be used as tests for the alkanol functional group, particularly the reaction with sodium and the esterification reaction. However, since the reaction with sodium is also given by any water-containing substance, and since the esterification reaction depends for its observation, on smell, they are not reliable as distinguishing tests for alkanols. A more dependable test is the action of ceric trioxonitrate(V) solution which produces a colour change, from yellow to red, with alkanols.

14.10 Phenols and Aromatic Alkanols

When the OH group is attached directly to a benzene nucleus the compound shows reactions that are quite different from those of alkanols. It becomes acidic in behaviour as it turns blue litmus scarlet, forms salt with alkalis and liberates carbon(IV) oxide from hydrogen trioxocarbonate(IV) salts (though not from trioxocarbonate(IV) salts). Such compounds are called phenols, e.g. phenol itself which is C_6H_5OH . The structure is:



Compounds containing the benzene nucleus and the hydroxyl group, with the hydroxyl group on a side chain and not on the benzene nucleus are aromatic alkanols, not phenols, e.g.



Chapter Summary

1. Alkanols have the general formula $C_nH_{2n+1}OH$. The functional group is the OH group.
2. Ethanol is prepared by fermentation.
3. Ethanol and methanol are soluble in water because of hydrogen-bonding.
4. They have fairly high boiling points when compared with the corresponding hydrocarbons, because of hydrogen bonding.
5. Ethanol and methanol react with sodium to give off hydrogen.
6. They are oxidized to alkanals and finally to alkanoic acids.
7. They are neutral. The exceptions are phenols which are acidic.
8. Dehydration of ethanol yields ethene at 180°C with excess concentrated tetraoxosulphate(VI) acid. With excess ethanol at 145°C ethylethoxide is formed.
9. Alkanols react with organic acids to form sweet smelling compounds called alkanoates (esters).
10. Monohydric alkanols can be classified into primary, secondary and

tertiary alkanols.

11. Polyhydric alkanols can be classified into dihydric, trihydric, etc. alkanols depending on the number of hydroxyl groups present in a molecule of the alkanol.

Assessment

1. What evidences are there for the molecular structure of ethanol?
2. (a) How would you prepare ethanol starting from starch?
(b) How and under what conditions does ethanol react with tetraoxosulphate(VI) acid?
(WAEC)
3. (a) Give the structure of all possible isomers of $C_5H_{11}OH$.
(b) Name each isomer.
4. (a) Write an equation for the reaction between sodium and ethanol.
(b) What type of chemical reaction is it?
(c) (i) What type of reaction occurs when ethanol reacts with ethanoic acid?
(ii) Write an equation to illustrate (c)(i) above.
5. Give an example each of
(a) monohydric alkanol.
(b) dihydric alkanol.
(c) trihydric alkanol.
6. Write an equation for the oxidation of ethanol using potassium tetraoxomanganate(VI).
7. Account for the following:
(i) ethanol is soluble in water.
(ii) ethanol has a fairly higher boiling point than propane.
8. State two uses of ethanol.
9. Write the structural formula of
(i) butan-2-ol.
(ii) propan-2-ol.
10. (i) Name the functional group in the compound
 $CH_3CH_2CH_2CH_2OH$
(ii) What is the effect of the functional group on litmus papers?
(iii) What effect has hydroxyl benzene (phenol) on (i) litmus paper,
(ii) solid sodium hydrogen trioxocarbonate(IV)?