

ETHERS

Saturated aliphatic ethers form a homologous series and correspond to a general molecular formula $(C_nH_{2n+1})_2O$ where n is equal to or greater than 1. They are characterized by the structural feature of an oxygen atom linking two hydrocarbon groups.

$R-O-R'$

Where R and R' may be similar or different. They may be aromatic or aliphatic and the names of the ethers correspond to the hydrocarbon groups present.

Examples

CH_3OCH_3 Methoxymethane $CH_3CH_2OCH_2CH_3$ Ethoxyethane

$(CH_3CH_2CH_2CH_2)_2O$ Butoxymethane $CH_3CH_2OCH_3$ Methoxyethane

$CH_3CH_2CH_2OCH_2CH_3$ Ethoxypropane

NOMENCLATURE

Ethers may be designated by the IUPAC system as hydrocarbon derivations. They are regarded as alkoxy derivatives of alkanes.

$CH_3CH_2OCH_2CH(CH_3)CH_2CH_3$ 2-Methylethoxybutane

$CH_3CH_2O(CH_2)_4CH_3$ Ethoxypentane

General properties

Physical states

At room temperature, ethers are colourless, neutral liquids with pleasant odours. The lower aliphatic ethers are highly flammable gases or volatile liquids.

Solubility

Ethers are less soluble in water than are the corresponding alcohols. Lower molecular weight ethers such as methoxymethane and methoxyethane are fairly soluble in water since the molecules are able to form hydrogen bonds with the water molecules but as the hydrocarbon content of the molecules increases, there is a rapid decline in solubility. They are miscible with most organic solvents.

Density

Most of the simple ethers are less dense than water, although the density increases with increasing relative molecular mass and some of the aromatic ethers are in fact denser than water

Boiling point

Low molecular mass ethers have a lower boiling point than the corresponding alcohols but those ethers containing alkyl radicals larger than four carbon atoms, the reverse is true. The boiling point of ethers tend to approximate those of hydrocarbons of same relative molecular mass from which it can be concluded that the molecules are not associated in the liquid phase as there are no suitably available hydrogen for association through hydrogen bonds,

Reactivity

Ethers are inert at moderate temperature. Their inertness at moderate temperatures leads to their wide use as reaction media

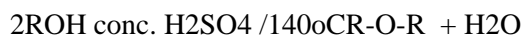
Simple ethers are not found commonly in nature but the ether linkage is present in such natural products as sugars, starches and cellulose

MANUFACTURE AND PREPARATION OF ETHERS

Partial dehydration of alcohols

Simple ethers are manufactured from alcohols by catalytic dehydration. The alcohol in excess and concentrated tetraoxosulphate(VI) acid is heated at a carefully maintained temperature of $140^\circ C$. This process is known as continuous etherification. If excess alcohol is not used, the temperature is as high as $170-180^\circ C$, further dehydration

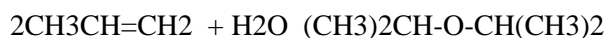
to yield alkene occurs



Examples

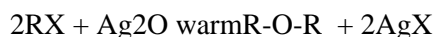


Controlled catalytic hydration of olefins



2-isopropoxypropane

From Haloalkanes and dry silver (I) oxide

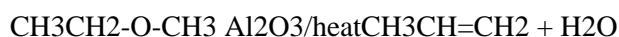


CHEMICAL REACTIONS

Ethers are relatively inert with regards to chemical reaction and in this regard they resemble the corresponding alkanes which carry no functional groups. However, the oxygen atom is sufficiently basic to undergo protonation in an acidic medium by the donation of a lone pair of electron, that is, it functions as a Lewis base. The protonated species is then susceptible to subsequent attack by a nucleophile. It is as a result of this phenomenon that ethers unlike alkanes do form salts with hydrogen chloride gas or concentrated tetraoxosulphate(vi) acid. Below are some of the reactions they undergo

Cleavage

Heat decomposes ethers especially in the presence of alumina catalysts to form olefins and water as principal products



Ethers undergo carbon –oxygen fission on heating with strong acids such as hydriodic, hydrobromic and nitric acids. This cleaves one or both of the carbon-oxygen linkages to form alkyl derivatives and in cases in which only one bond is cleaved, an alcohol is one of the products



Autoxidation

In the presence of oxygen, ethers undergo self-oxidation to unstable peroxides and this reaction may create the danger of explosion in stored ether. For this reason, ethers should be stored in dark bottles and should contain an antioxidant



CYCLIC ETHERS

Ethylene Oxide (Oxirane)

Several cyclic ethers are of considerable importance and interest. The simplest of these is ethylene oxide (epoxyethane or oxirane)

O

It is made industrially by oxidation of ethylene with air over a silver catalyst



Ethylene oxide is used as an intermediate in the hydrolytic manufacture of ethylene glycol

Ethylene oxide is used in the preparation of nonionic emulsifying agents, plastics, plasticizers and several synthetic textiles

Ethylene oxide is used as a gaseous sterilizing agent

