You probably have heard of the term “alkanes” before but may be wondering what they are. We often encounter Alkanes in our daily lives – natural gas, liquid petroleum gas (LPG), propellants, fuels, and others. Today, we shall discuss what alkanes are and some of the reactions involving alkanes.

What are Alkanes?

As mentioned in Organic Chemistry – An Introduction, alkanes are hydrocarbons with a general formula of C_nH_{2n+2}. To be more specific, alkanes are saturated aliphatic hydrocarbons, which means that they only contain carbon and hydrogen atoms. Covalent bonds join adjacent carbon atoms. We have also mentioned that alkanes have a suffix –ane.

Here are some of the simpler alkanes that we commonly encounter.

n	Name	Molecular formula	Structural formula	M_r	Melting point / °C	Boiling point / °C	Physical state (r.t.p)
1	Methane	CH_4	CH_4	16	-182	-162	Gas
2	Ethane	C_2H_6	CH_3CH_3	30	-183	-89	Gas
3	Propane	C_3H_8	$CH_3CH_2CH_3$	44	-188	-42	Gas
4	Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	58	-138	-0.5	Gas
5	Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	72	-130	36	Liquid
6	Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	86	-95	69	Liquid

Alkanes with three or more carbon atoms exhibit isomerism. For example, propane has two constitutional isomers ($CH_3CH_2CH_2CH_3$ and $CH_3CHCH_3CH_3$) whereas butane has three constitutional isomers ($CH_3CH_2CH_2CH_3$, $CH_3CHCH_3CH_2CH_3$, and $CH_3C(CH_3)_2CH_3$).

What are Cycloalkanes?

Cycloalkanes are saturated alicyclic hydrocarbons – this means that they have a ring of carbon atoms. Unlike alkanes, cycloalkanes have a general formula of C_nH_{2n}. They are technically different from alkanes and contain the prefix cyclo– to distinguish them from the aliphatic alkanes.

Here are some of the simpler cycloalkanes that we often see.

n	Name	Molecular formula	Structural formula	M_r	Melting point / °C	Boiling point / °C	Physical state (r.t.p)
3	Cyclopropane	C_3H_6	△	42	-128	-33	Gas
4	Cyclobutane	C_4H_8	□	56	-91	12.5	Gas
5	Cyclopentane	C_5H_{10}	⬠	70	-94	49	Liquid
6	Cyclohexane	C_6H_{12}	⬡	84	6.5	81	Liquid

Properties of Alkanes

Melting and boiling points

Alkanes' melting and boiling points differ based on whether it is a straight-chained or branched-chained alkane.

As the number of carbons in the hydrocarbon chain increases, more energy is needed to overcome the stronger instantaneous dipole-induced dipole (id-id) interactions between molecules. As such, the boiling point of the straight-chained alkanes increases. Therefore, the first four alkanes are gases at room temperature, whereas the next thirteen are liquids.

The increasing trend is also seen in the melting points of straight-chained alkanes. However, alkanes with odd-number carbon atoms tend to have a lower melting point than expected.

Branched-chained alkanes often have lower melting points than straight-chained alkanes. This is because they have less surface area of contact between molecules since they are more spherical. As such, there is a decrease in the strength of id-id interactions.

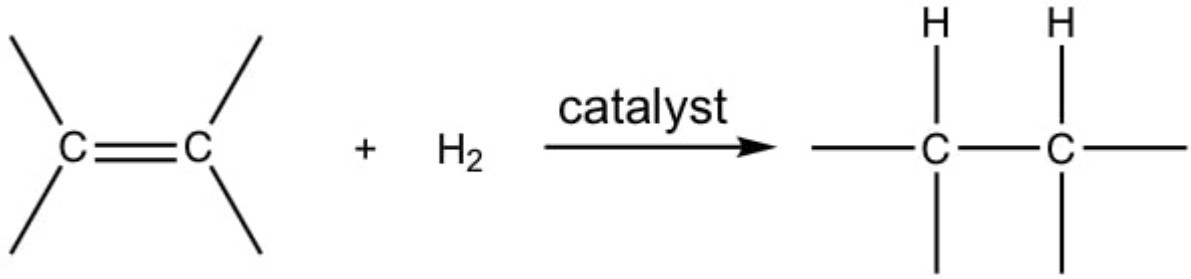
Other physical properties

Alkanes are colourless, non-polar molecules. They are insoluble in polar solvents but are soluble in non-polar solvents. This is due to the energy released between water molecules and alkane molecules being insufficient to overcome the strong hydrogen bonds between water molecules.

On top of that, alkanes are less dense than water. They also become more viscous and less flammable with more carbon atoms.

Preparing Alkanes

Alkanes are produced by reducing alkenes. This is done by heating the alkene with hydrogen gas in the presence of a nickel catalyst. However, we can also reduce alkenes using a platinum or palladium catalyst. This process is also known as hydrogenation.



Reactions

Combustion

Alkanes react with oxygen in a combustion reaction, with smaller alkanes igniting more easily. With a limited supply of oxygen, the incomplete combustion of alkanes will produce carbon monoxide (CO) and water (H_2O). However, with excess oxygen, the complete combustion of alkanes will produce carbon dioxide (CO_2) and water (H_2O).

Combustion reactions are exothermic – more energy is produced with more carbon atoms. As alkanes are easily burnt, many of them are used as fuels. One such example is methane (CH_4), which is used because it is clean – little soot (carbon) is formed when methane is burnt.

The complete combustion of alkane has the general equation:

$C_xH_y + (x + y/4)\ O_2 \rightarrow xCO_2 + y/2\ H_2O$

Halogenoalkanes

Alkanes form halogenoalkanes when reacted with halogens in a free-radical substitution reaction. This is done under UV light or high temperatures, substituting hydrogen atoms with halogen atoms in the alkanes.

We will be using the chlorination of ethane as an example of a free-radical substitution

reaction.

In the initiation step, free radicals Cl• are generated. This occurs when UV light or high temperatures provides energy for the homolytic fission of the Cl–Cl bond.

$Cl–Cl \rightarrow 2Cl•$

There is a chain reaction involving the consumption and generation of Cl• radicals in the propagation step. This is due to the consumption of a Cl• radical in one step and the generation of another Cl• radical in the next step.

$CH_3CH_3 + Cl• \rightarrow CH_3\dot{C}H_2 + HCl$

$Cl_2 + CH_3\dot{C}H_2 \rightarrow CH_3CH_2Cl + Cl•$

In the termination step, free radicals continue to be consumed but are no longer generated. There are many possible termination steps:

$Cl• + Cl• \rightarrow Cl_2$

$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \rightarrow CH_3(CH2)_2CH_3$

$CH_3\dot{C}H_2 + Cl• \rightarrow CH_3CH_2Cl$

This results in the overall equation of $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$.

Once a single free radical is formed, the chain reaction sequence allows many product molecules to be produced. That said, the reaction is limited to monosubstitution and more than one hydrogen atom in the alkane molecule. To visualise this, let us use the chlorination of methane as an example:

Monosubstitution	$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
Disubstitution	$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$
Trisubstitution	$CH_2Cl + Cl_2 \rightarrow CHCl_3 + HCl$
Tetrasubstitution	$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Reactivity and Substitution

As we know, the reactivity of halogens decreases down the group. This makes fluorine and

iodine unsuitable for free-radical substitution – fluorine is too reactive, whereas iodine is too unreactive. In addition, down the group, as halogens have a larger atomic radius, the energy released when the H–X bond is formed is less than that needed to break the C–H bonds in an alkane. This makes the first propagation step more endothermic, and thus it becomes increasingly harder to substitute the halogen.

When halogens substitute hydrogen atoms on different carbon atoms, other products are formed. However, this is more commonly seen in higher alkanes.

Occurrence of Alkanes

When I first learnt about this, I was a little surprised – we can also find alkanes in the atmospheres of other planets! Jupiter, Saturn, Uranus, and Neptune have a small portion of methane and ethane in their atmospheres. Saturn's largest moon, Titan, often encounters rains made of liquid methane.

A small amount of gaseous alkanes can be found in our atmosphere on Earth – namely methane. This is partially due to air pollution, which is formed when we burn fossil fuels (alkanes). However, hydrocarbons can be found deep within Earth's surface from the fossils of dead marine life over millions of years ago.