AN INTRODUCTION TO

THE CHEMISTRY OF ALKANES

ALKANES

General

members of a homologous series

general formula is C_nH_{2n+2} - for non-cyclic alkanes

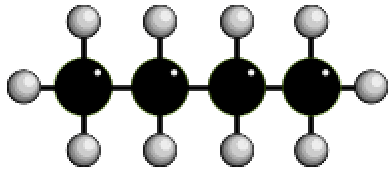
saturated hydrocarbons - all carbon-carbon bonding is single

bonds are spaced tetrahedrally about carbon atoms.

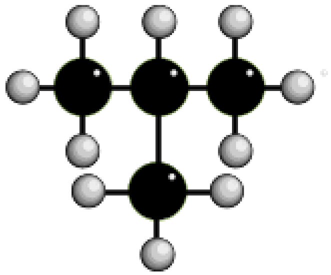
Isomerism

the first example of structural isomerism occurs with C_4H_{10}

BUTANE



2-METHYLPROPANE

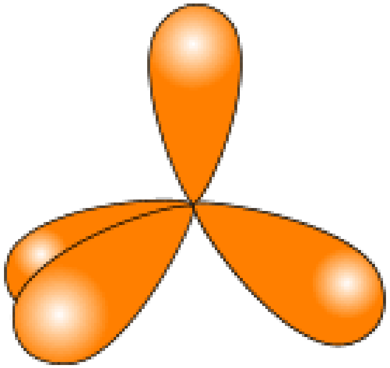


Structural isomers have the SAME MOLECULAR FORMULA BUT DIFFERENT STRUCTURAL FORMULA

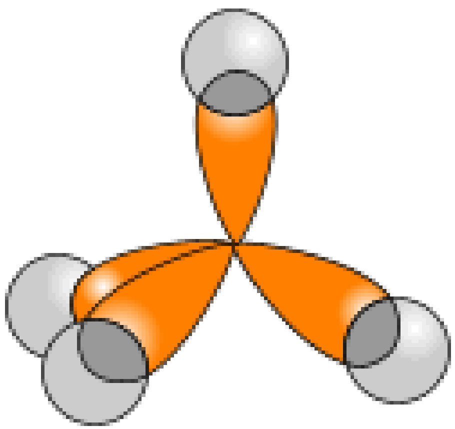
They possess different physical properties such as boiling point, melting point and density

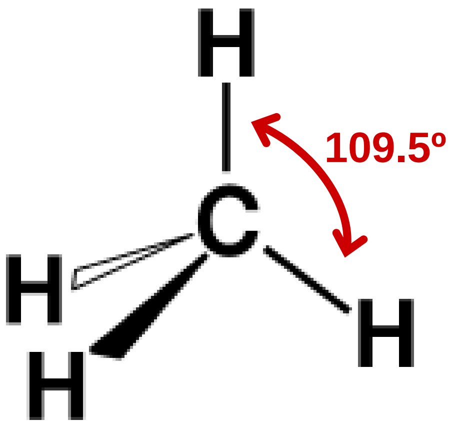
THE Bonding & STRUCTURE OF ALKANES

In ALKANES, the four sp^3 orbitals of carbon repel each other into a **TETRAHEDRAL** arrangement with bond angles of 109.5º.



Each sp^3 orbital in carbon overlaps with the 1s orbital of a hydrogen atom to form a C-H bond.





PHYSICAL PROPERTIES OF ALKANES

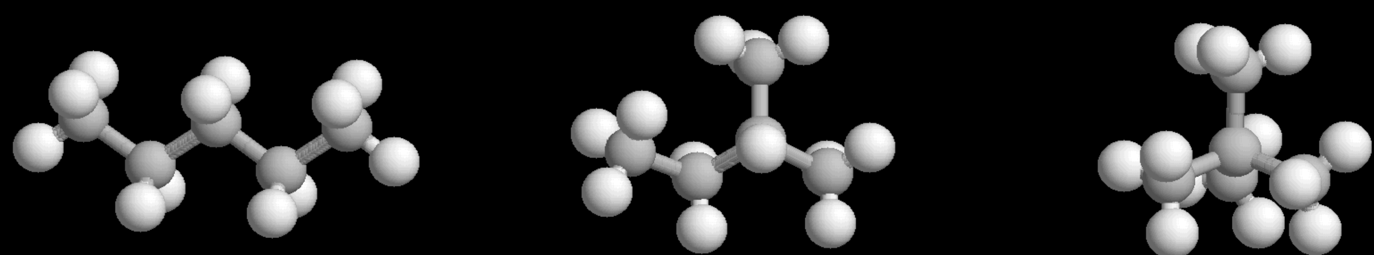
Boiling point increases as they get more carbon atoms in their formula
more atoms = greater intermolecular Van der Waals’ forces
greater intermolecular force = more energy to separate the molecules
greater energy required = higher boiling point

CH_4 (-161°C) C_2H_6 (-88°C) C_3H_8 (-42°C) C_4H_{10} (-0.5°C)

difference gets less - mass increases by a smaller percentage

Straight chains molecules have greater interaction than branched

STRUCTURAL ISOMERS OF C_5H_{12}



HIGHEST BOILING POINT LOWEST BOILING POINT

“The greater the branching, the lower the boiling point”

PHYSICAL PROPERTIES OF ALKANES

Melting point general increase with molecular mass
the trend is not as regular as that for boiling point.

Solubility alkanes are **non-polar** so are **immiscible with water**
they are **soluble in most organic solvents**.

CHEMICAL PROPERTIES OF ALKANES

Introduction

- **fairly unreactive; (old family name, paraffin, meant little reactivity)**
- **have relatively strong, almost NON-POLAR, SINGLE covalent bonds**
- **they have no real sites that will encourage substances to attack them**

Combustion

- **make useful fuels - especially the lower members of the series**
- **react with oxygen in an exothermic reaction**

complete combustion $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

incomplete combustion $CH_4(g) + 1\tfrac{1}{2}O_2(g) \longrightarrow CO(g) + 2H_2O(l)$

the greater the number of carbon atoms, the more energy produced
BUT the greater the amount of oxygen needed for complete combustion.

Handy tip

When balancing equations involving **complete combustion**, remember...
every carbon in the original hydrocarbon gives one carbon dioxide and
every two hydrogen atoms gives a water molecule.

Put the numbers into the equation, count up the O's and H's on the RHS
of the equation then balance the oxygen molecules on the LHS.

POLLUTION

Processes involving combustion give rise to a variety of pollutants...

power stations — SO_2 emissions produce acid rain
internal combustion engines — CO, NOx and unburnt hydrocarbons

Removal

SO_2 — react effluent gases with a suitable compound (e.g. CaO)
CO and NOx — pass exhaust gases through a catalytic converter

Catalytic converters

In the catalytic converter ... CO is converted to CO_2
NOx are converted to N_2
Unburnt hydrocarbons are converted to CO_2 and H_2O

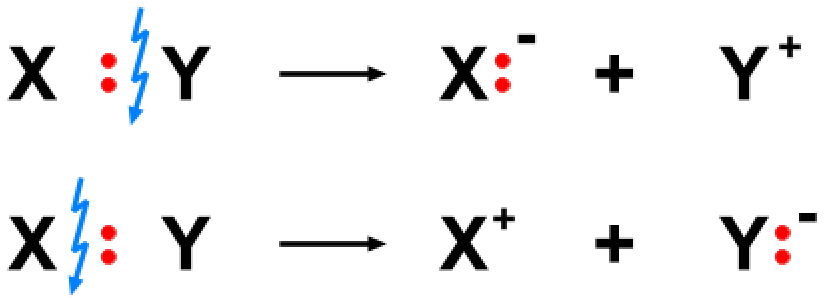
e.g. $$2NO + 2CO \longrightarrow N_2 + 2CO_2$$

- catalysts are made of finely divided rare metals Rh, Pd, Pt
- leaded petrol must not pass through the catalyst as the lead deposits on the catalyst's surface and "poisons" it, thus blocking sites for reactions to take place.

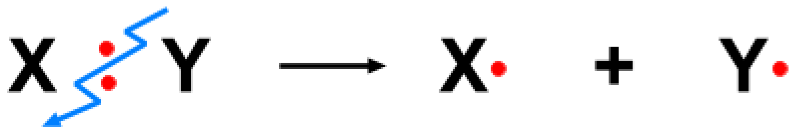
BREAKING COVALENT BONDS

There are 3 ways to split the shared electron pair in an unsymmetrical covalent bond.

UNEQUAL SPLITTING
produces **IONS**
known as **HETEROLYSIS** or
HETEROLYTIC FISSION



EQUAL SPLITTING
produces **RADICALS**
known as **HOMOLYSIS** or
HOMOLYTIC FISSION



- **If several bonds are present the weakest bond is usually broken first**
- **Energy to break bonds can come from a variety of energy sources - heat / light**
- **In the reaction between methane and chlorine either can be used, however...**
- **In the laboratory a source of UV light (or sunlight) is favoured.**

FREE RADICALS

TYPICAL PROPERTIES

- reactive species (atoms or groups) which possess an unpaired electron
- their reactivity is due to them wanting to pair up the single electron
- formed by homolytic fission (homolysis) of covalent bonds
- formed during the reaction between chlorine and methane
- formed during thermal cracking
- involved in the reactions taking place in the ozone layer

CHLORINATION OF METHANE

Reagents chlorine and methane

Conditions UV light or sunlight - heat is an alternative energy source

Equation(s)

$CH_4(g) + Cl_2(g) \longrightarrow HCl(g) + CH_3Cl(g)$ chloromethane

$CH_3Cl(g) + Cl_2(g) \longrightarrow HCl(g) + CH_2Cl_2(l)$ dichloromethane

$CH_2Cl_2(l) + Cl_2(g) \longrightarrow HCl(g) + CHCl_3(l)$ trichloromethane

$CHCl_3(l) + Cl_2(g) \longrightarrow HCl(g) + CCl_4(l)$ tetrachloromethane

Mixtures free radicals are very reactive - they are trying to pair their electron with sufficient chlorine, every hydrogen will eventually be replaced.

Mechanism Mechanisms portray what chemists think is going on in the reaction, whereas an equation tells you the ratio of products and reactants.

Chlorination of methane proceeds via **FREE RADICAL SUBSTITUTION** because the methane is **attacked by free radicals** resulting in **hydrogen atoms being substituted** by chlorine atoms.

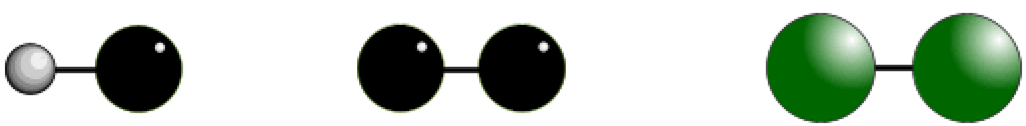
The process is a **chain reaction**.
In the propagation step, one radical is produced for each one used

CHLORINATION OF METHANE

Initiation $Cl_2 \longrightarrow 2Cl\bullet$ **RADICALS CREATED**

The single dots represent UNPAIRED ELECTRONS

During initiation, the WEAKEST BOND IS BROKEN as it requires less energy. There are three possible bonds in a mixture of alkanes and chlorine.



412 **348** **242**

Average bond enthalpy kJ mol^{-1}

The Cl-Cl bond is broken in preference to the others as it is the weakest and requires requires less energy to separate the atoms.

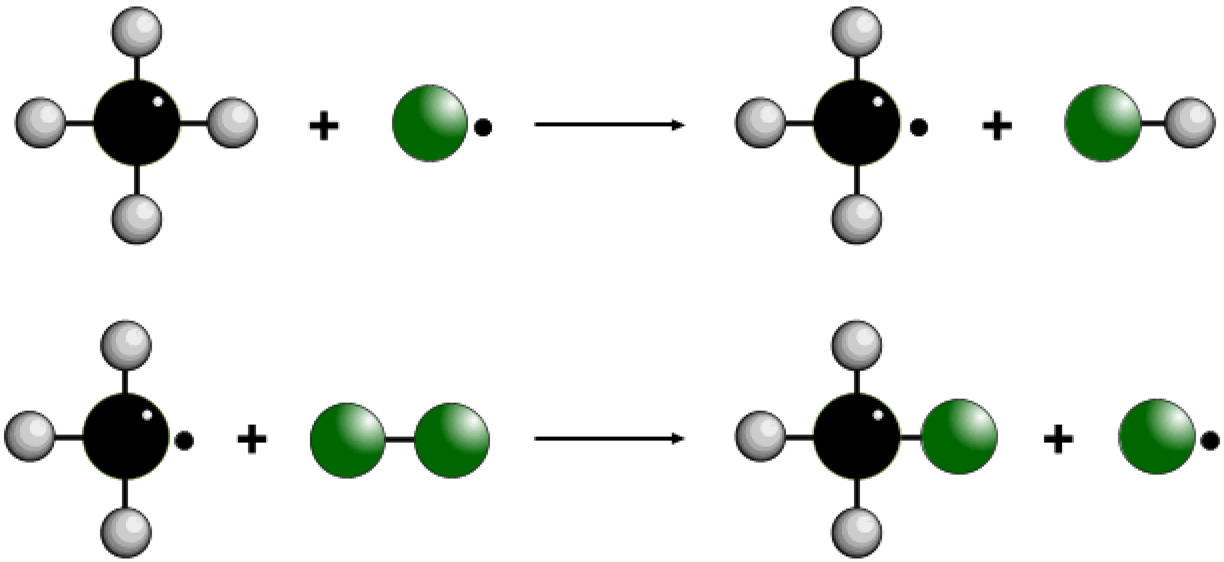
CHLORINATION OF METHANE

Propagation

$Cl\bullet + CH_4 \longrightarrow CH_3\bullet + HCl$

$Cl_2 + CH_3\bullet \longrightarrow CH_3Cl + Cl\bullet$

RADICALS USED and then **RE-GENERATED**



Free radicals are very reactive because they want to pair up their single electron.
They do this by abstracting a hydrogen atom from methane; a methyl radical is formed
The methyl radical is also very reactive and attacks a chlorine molecule
A chlorine radical is produced and the whole process can start over again

CHLORINATION OF METHANE

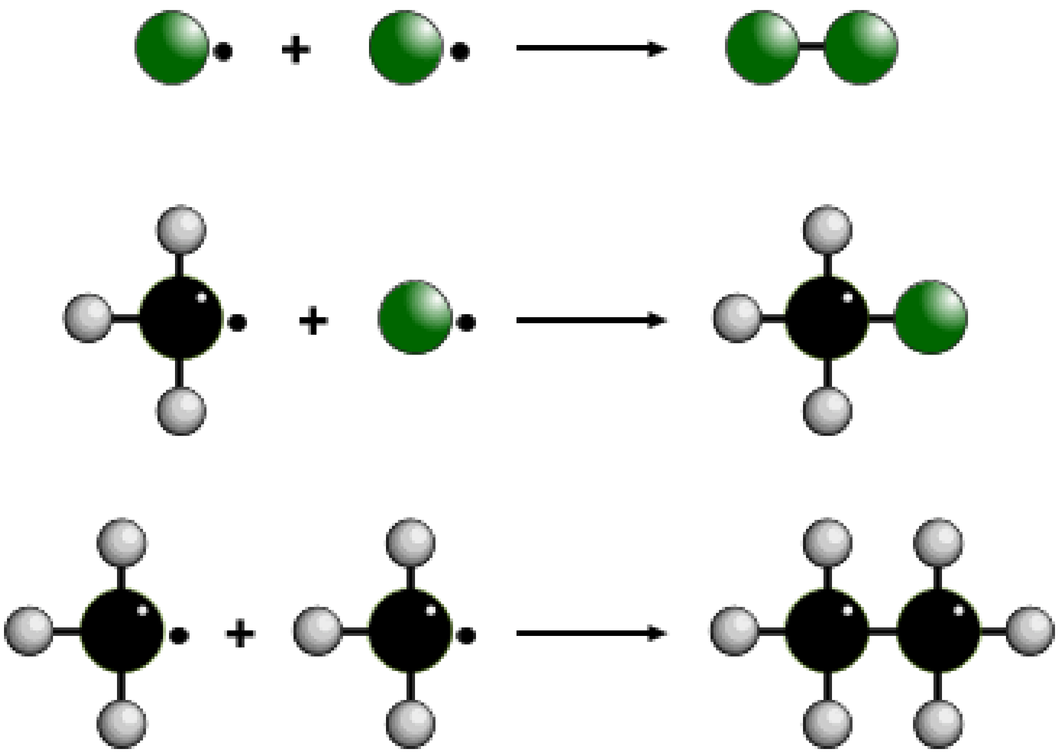
Termination

$Cl\bullet + Cl\bullet \longrightarrow Cl_2$

$Cl\bullet + CH_3\bullet \longrightarrow CH_3Cl$

$CH_3\bullet + CH_3\bullet \longrightarrow C_2H_6$

RADICALS REMOVED



Removing the reactive free radicals brings an end to the reaction.

This is not very likely at the start of the reaction because of their low concentration.

CHLORINATION OF METHANE

OVERVIEW

Initiation	$Cl_2 \longrightarrow 2Cl\bullet$	radicals **created**
Propagation	$Cl\bullet + CH_4 \longrightarrow CH_3\bullet + HCl$ $Cl_2 + CH_3\bullet \longrightarrow CH_3Cl + Cl\bullet$	radicals **used** and then **re-generated**
Termination	$Cl\bullet + Cl\bullet \longrightarrow Cl_2$ $Cl\bullet + CH_3\bullet \longrightarrow CH_3Cl$ $CH_3\bullet + CH_3\bullet \longrightarrow C_2H_6$	radicals **removed**

Summary

Due to lack of reactivity, alkanes need a very reactive species to persuade them to react

Free radicals need to be formed by homolytic fission of covalent bonds

This is done by shining UV light on the mixture (heat could be used)

Chlorine radicals are produced because the Cl-Cl bond is the weakest

You only need one chlorine radical to start things off

With excess chlorine you get further substitution and a mixture of chlorinated products

CHLORINATION OF METHANE

Initiation

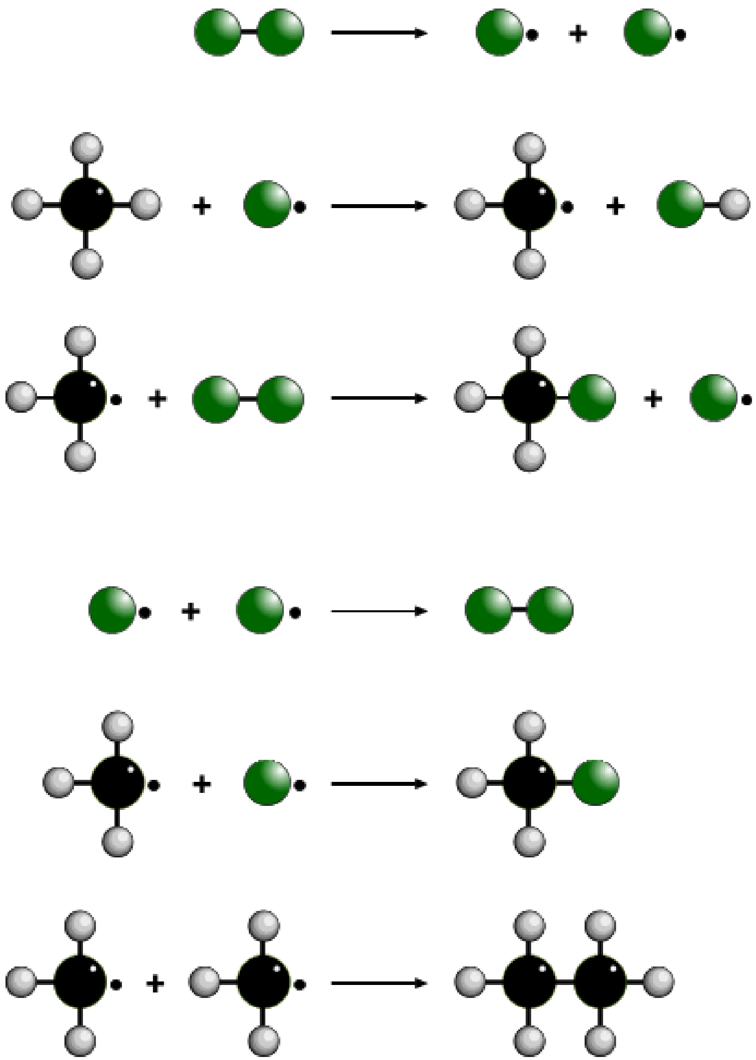
RADICALS PRODUCED

Propagation

RADICALS USED AND REGENERATED

Termination

RADICALS REMOVED



CHLORINATION OF METHANE

Further propagation

If excess chlorine is present, further substitution takes place
The equations show the propagation steps for the formation of...

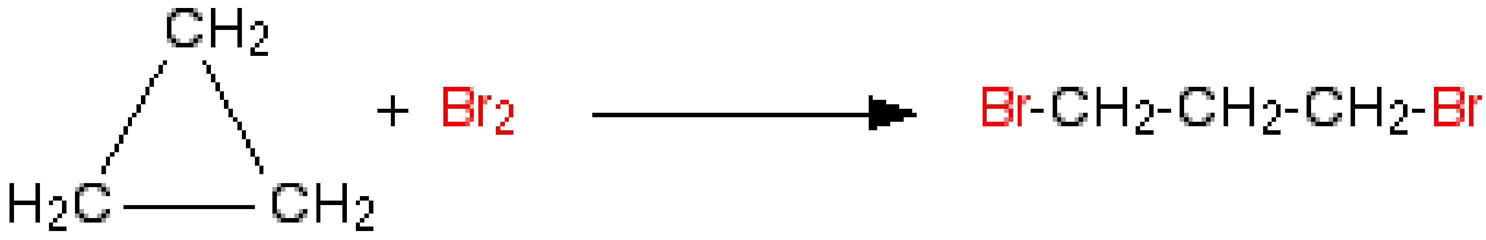
dichloromethane	$Cl\bullet + CH_3Cl$	——>	$CH_2Cl\bullet + HCl$
	$Cl_2 + CH_2Cl\bullet$	——>	$CH_2Cl_2 + Cl\bullet$
trichloromethane	$Cl\bullet + CH_2Cl_2$	——>	$CHCl_2\bullet + HCl$
	$Cl_2 + CHCl_2\bullet$	——>	$CHCl_3 + Cl\bullet$
tetrachloromethane	$Cl\bullet + CHCl_3$	——>	$CCl_3\bullet + HCl$
	$Cl_2 + CCl_3\bullet$	——>	$CCl_4 + Cl\bullet$

Mixtures **Because of the many possible reactions there will be a mixture of products.**
Individual haloalkanes can be separated by fractional distillation.

Cycloalkanes

The reactions of the cycloalkanes are generally just the same as the alkanes, with the exception of the very small ones - particularly cyclopropane.

*The ring is broken because cyclopropane suffers badly from **ring strain**. The bond angles in the ring are 60° rather than the normal value of about 109.5° when the carbon makes four single bonds.*



CRACKING

Involves the breaking of C-C bonds in alkanes
Converts heavy fractions into higher value products

CATALYTIC **proceeds via a carbocation (carbonium ion) mechanism**

CATALYTIC

SLIGHT PRESSURE

HIGH TEMPERATURE ... 450°C – 500 ^{o}C

ZEOLITE CATALYST

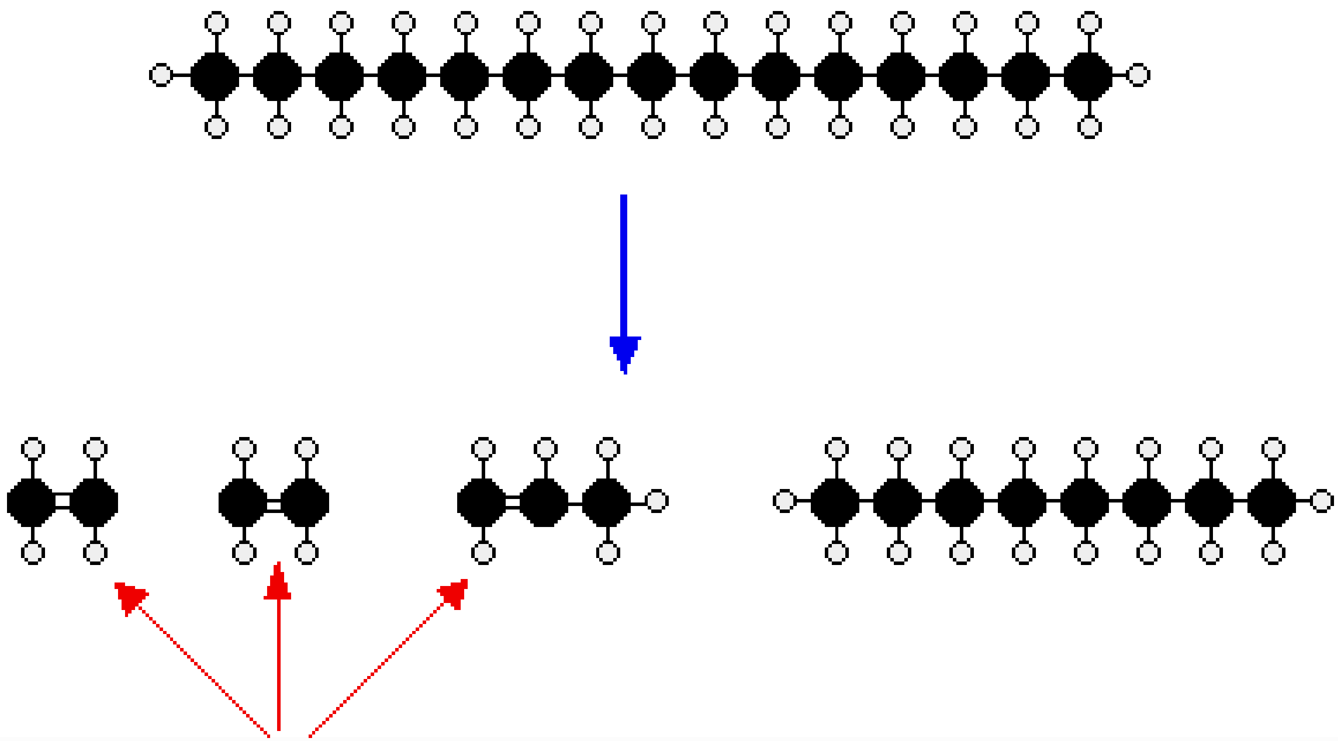
PRODUCES BRANCHED AND CYCLIC ALKANES, AROMATIC HYDROCARBONS
USED FOR **MOTOR FUELS**

ZEOLITES are crystalline aluminosilicates; clay like substances

One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be:

$$C_{15}H_{32} \longrightarrow 2C_2H_4 + C_3H_6 + C_8H_{18}$$

ethene propene octane



Notice the double bonds formed.

Catalytic Reforming: *Formation of benzene from alkane*