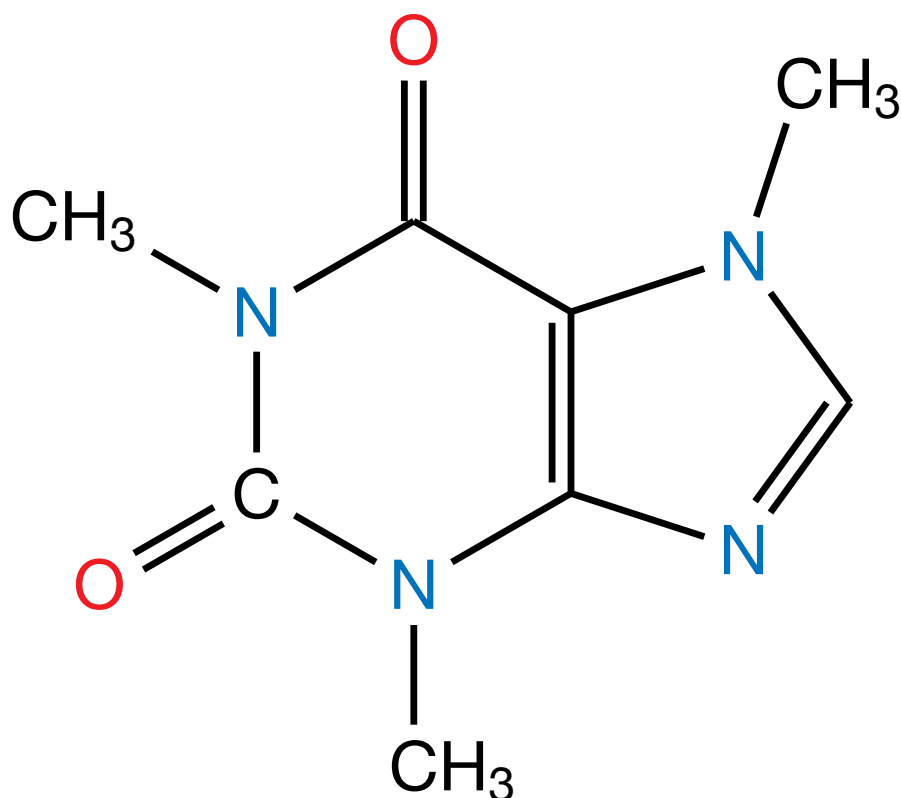


Organic Chemistry



1,3,7-trimethylpurine-2,6-dione

or

Caffeine

Chapters 8 to 12

1 Functional Groups

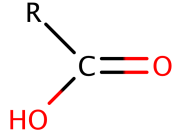
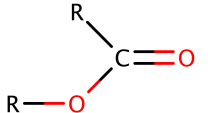
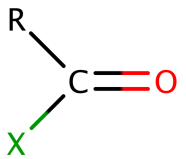
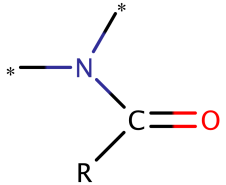
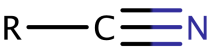
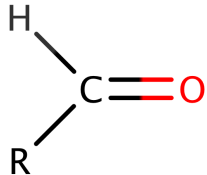
1.1 Overview

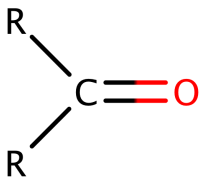
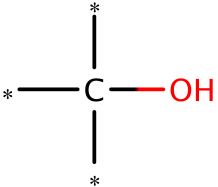
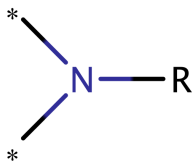
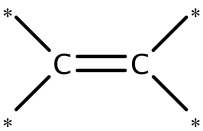
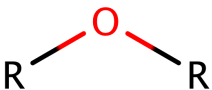
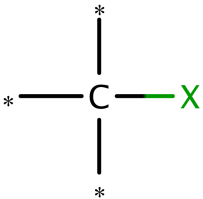
Functional groups are the main determinant of the chemical properties of a molecule. Molecules with the same functional group are of the same *family* and similar *chemical properties*.

Functional groups can be any size — the ketone functional group is just an oxygen double-bonded to a carbon atom in any position, while the carboxylic acid functional group has a more complex structure.

1.2 Basic Functional Groups

Note that this table is ordered based on the *priority* of the functional group, in terms of where it appears in an IUPAC-named chemical compound.

Name	Prefix Form	Suffix Form	Structure
Carboxylic Acid	carboxy-*	*-oic acid	
Ester	-	*-oate	
Acyl Halide	halocarbonyl-*	*-oyl halide	
Amide	carbamoyl-*	*-amide	
Nitrile	cyano-*	*-nitrile	
Aldehyde	formyl-*	*-al	

Ketone	oxo-*	*-one	
Alcohol	hydroxy-*	*-ol	
Amine	amino-*	*-amine	
Alkene	alkenyl-*	*-ene	
Ether	alkoxy-*	-	
Alkyl Halide	halogen-*	-	

2 Isomers

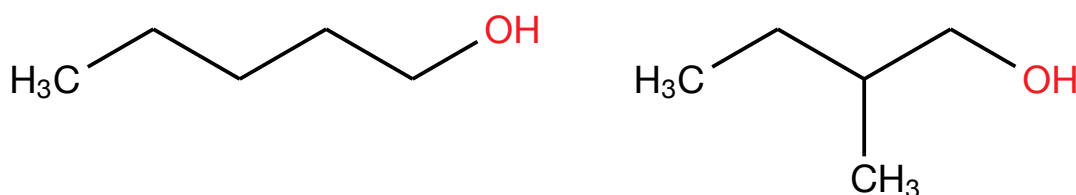
2.1 Overview

Isomers are molecules that share the same structural formula, yet exist in different forms. The two main forms of isomerism are structural isomerism and stereoisomerism. In both cases, the molecular formula of the compounds is the same, while the chemical and physical properties may differ greatly.

2.2 Structural Isomerism

2.2.1 Chain Isomerism

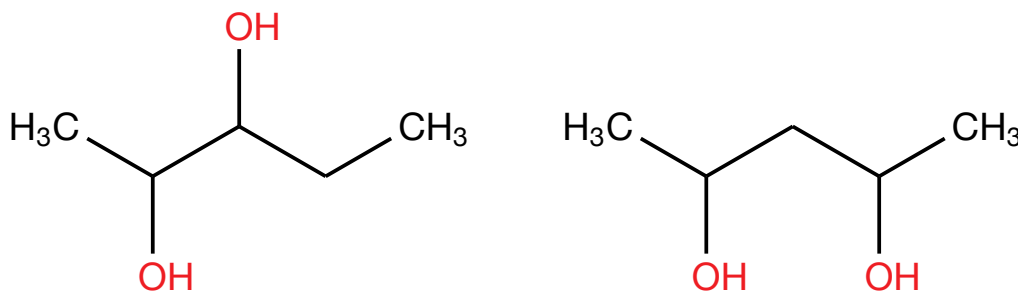
In chain isomerism, molecules have the same functional groups, except they are placed in different positions along the carbon chain. Chain isomers typically have similar chemical properties, but different physical properties (since the shape of the carbon chain can determine the strength of intermolecular interactions).



Pentanol and 3-methylbutan-1-ol are chain isomers.

2.2.2 Positional Isomerism

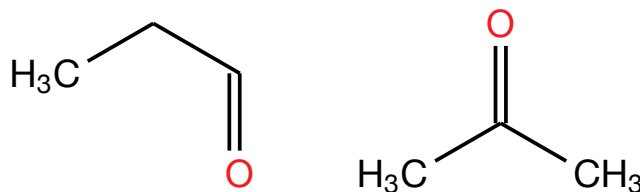
Positional isomers have the same arrangement of carbon chains, and the same functional groups. However, said functional groups are placed at different positions.



Butan-2,3-diol and butan-2,4-diol are positional isomers.

2.2.3 Functional Group Isomerism

This is somewhat a misnomer, since it is exactly the opposite of what it seems to intuit. Functional group isomers share only their molecular formulas; the carbon chain, the functional groups, etc. are all different.



Propanal and acetone are functional group isomers.

2.3 Stereoisomerism

2.3.1 Overview

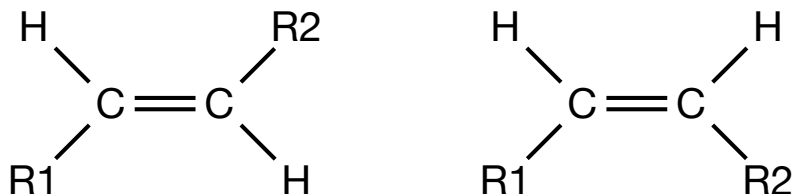
Stereoisomers of molecules have the same structure and functional groups, but those groups are arranged in a spatially differing way. The main forms of stereoisomerism are cis/trans (or E/Z) isomerism, and optical isomerism.

Note that for certain cis/trans (E/Z) isomers, the trans (or E) variant can 'pack' better, resulting in a higher melting point. This doesn't affect the boiling point, since the molecules are too far apart in the gaseous phase for this to matter.

Additionally, the presence of *intramolecular* (within the same molecule) hydrogen bonds can also be a factor, since it reduces the strength of *intermolecular* hydrogen bonds. Other than these, the chemical and physical properties of stereoisomers are mostly the same.

2.3.2 Cis/Trans Isomerism

Only alkenes can exhibit stereoisomerism, due to the C=C bond that restricts rotation along its axis. This is because of the π -bonds that only bond at 180° intervals. At these positions, it forms the cis and trans isomers.

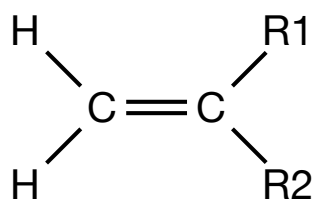


The molecule on the left is the *trans* isomer, while the one on the right is the *cis* isomer. *trans* is from Latin, meaning *other side*, while *cis* obviously means *same side*. In the former, the larger groups are on opposite sides of the alkene double bond, while in the latter, the larger groups are on the same side. Note that these *groups* do not necessarily have to be functional groups — they can be as large or as simple as one wishes.

When naming cis/trans isomers, the qualifier *cis* or *trans* is placed before the stem name, like so:

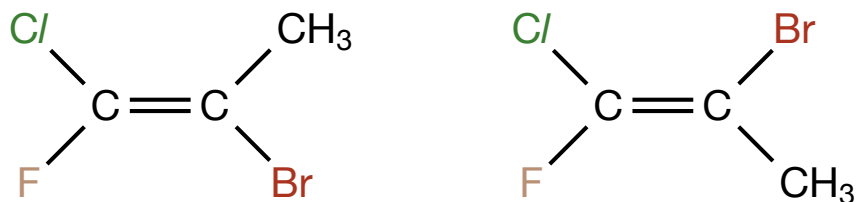
- cis-but-2-ene
- trans-but-2-ene

Note that cis/trans isomerism is not applicable to molecules where identical groups are attached to the any one carbon atom, since there is a line of symmetry going along the plane of the double bond.



2.3.3 E/Z Isomerism

E/Z is thought of as the more comprehensive, general form of cis/trans. Consider the alkene below, with two variants due to the lack of a plane of symmetry:



It has 4 distinct substituents, and thus a cis/trans designation cannot be used. Behold, E/Z isomerism. At its core it is simply another method of handling alkene isomers that works for more general forms of molecules.

It follows a scheme of priorities (Cahn-Ingold-Prelog, or CIP), which are determined as such:

- i. The group with the largest atomic mass *directly attached* to the alkene's carbon has the highest priority.
- ii. In the event of a tie, look at the atoms directly attached to *that* offending atom. Use the previous rule, favouring higher priority atoms, to tiebreak. Double bonds are counted twice.
- iii. Recursively evaluate the previous rule with attached atoms, to continue the tiebreaking process.

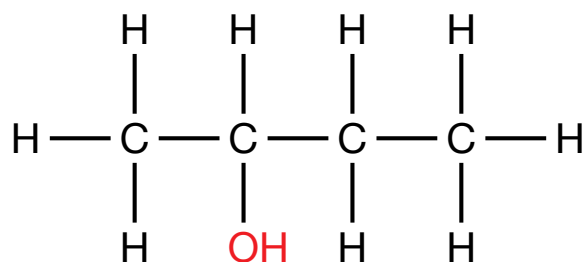
The above scheme should be used to find the two highest-priority groups attached to the alkene, after which, if the two groups are attached on the same side of the alkene, then the molecule is the *Z* isomer, and it is known as the *E* isomer if the reverse is true.

E and Z come from the German *entgegen* and *zusammen*, *opposite* and *together* respectively.

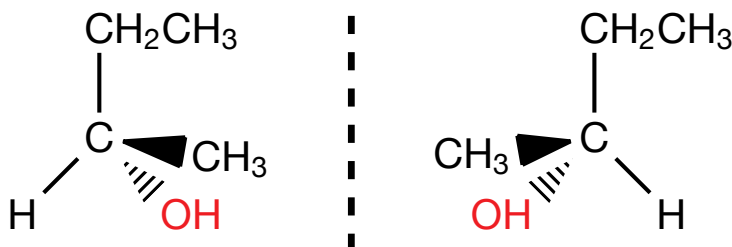
2.3.4 Optical Isomerism

Due to the 3-dimensional tetrahedral nature of a carbon atom, if there are 4 *distinct* substituents, two non-superimposable mirror images can exist, resulting from a lack of any plane of symmetry. Such carbons are called *chiral carbons*, and are the *chiral centres* of the molecule. A molecule can have multiple chiral centres.

Consider butan-2-ol below. Carbon 2, with the OH group, has 4 different groups attached to it. As such, it is a chiral carbon.



Indeed, it can take the form of 2 non-superimposable mirror images, that are differentiated by the adjacency of 2 of the 4 groups bonded to the chiral carbon. As can be seen, these two mirror images cannot be rearranged into the other, and are distinct — these are called *enantiomers*.



The solid wedge indicates a bond coming out of the plane of the paper, while the dashed wedge indicates a bond going into the plane.

Optical isomers have identical physical properties, except for their treatment of plane-polarised light (this is where the light wave is only oscillating along one plane). One of the isomers will rotate this light clockwise, while the other will rotate it counterclockwise. The magnitude of both rotations are the same.

If equal amounts of each enantiomer are present in a solution, it is called a *racemic mixture*, and the net rotation of plane polarised light will be 0, for obvious reasons.

Enantiomers usually have identical chemical properties, except for certain interactions that require a certain spatial orientation to work, such as proteins, that can only work with one of the optical isomers.

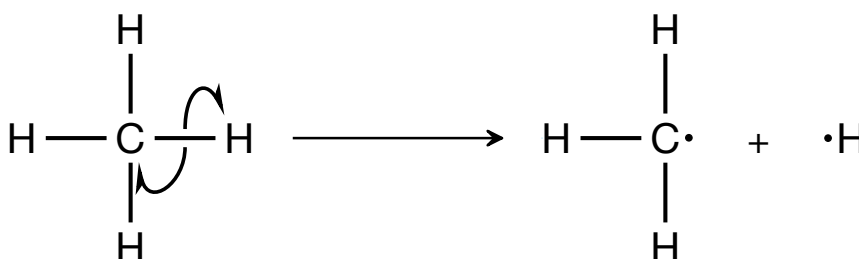
3 Reaction Mechanisms

3.1 Bond Breaking

3.1.1 Homolytic Fission

Homolytic fission involves the splitting of a single bond, with an equal (*homo*) distribution of the two electrons of the aforementioned bond. This results in the formation of radicals, since now both atoms from the bond will have unpaired electrons.

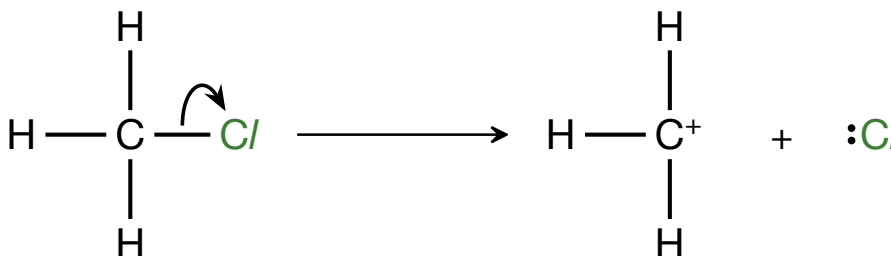
The movement of these single electrons is represented with single-hooked arrows. The arrow starts from the bond line, and points towards the target atom receiving the electron.



The homolytic fission of CH_4 , forming CH_3 and H radicals.

3.1.2 Heterolytic Fission

As the name implies, heterolytic fission is the opposite; it distributes both electrons of the bond to a single atom, which usually results in the formation of ions. The transfer here is represented using a full (double-hooked) arrow.



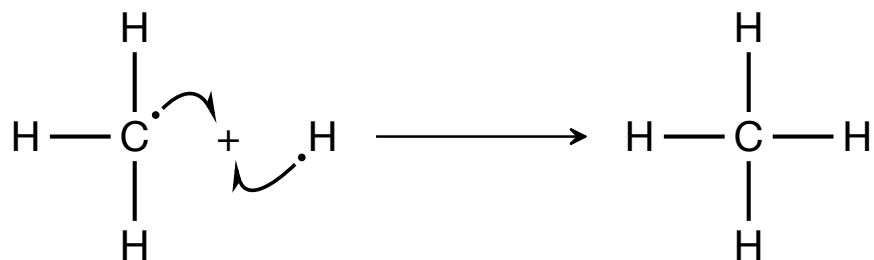
The heterolytic fission of CH_3Cl , resulting in CH_3^+ and Cl^- ions

3.2 Bond Forming

3.2.1 Single Electrons

Bond forming is essentially the reverse of bond breaking, and hence the same notations apply — single-hooked arrow for the movement of single electrons, and double-hooked arrows for the movement of an electron pair.

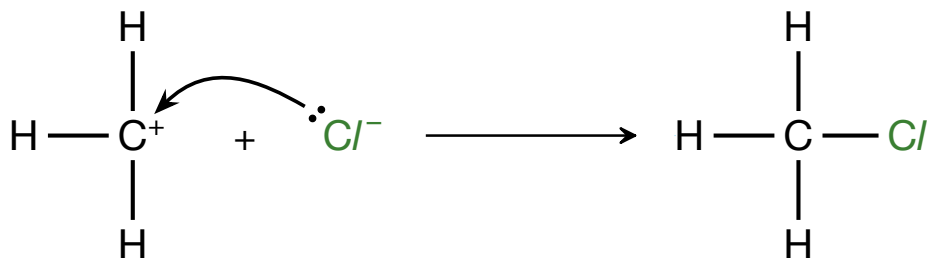
In this case, two single electrons from each atom contribute to the new bond.



The formation of a bond between CH_3 and H radicals to form CH_4 .

3.2.2 Electron Pairs

Electron pairs usually come from negatively charged radicals or lone pairs, although this is not a rule. Both electrons come from a single source to form a bond, but this is *not* a dative bond — it is simply a normal bond.



The formation of a bond between CH_3 and Cl^- radicals, to form CH_3Cl .

3.3 Electrophiles and Nucleophiles

3.3.1 Electrophiles

Electrophiles are electron-deficient species that accept an electron pair from a nucleophile donor. Most electrophiles either have a positive charge, or contain an atom that is polarised and thus has a partial positive charge.

Examples of electrophiles include CH_3^+ , Br^+ , NO_2^+ , polarised Br_2 , and HBr .

3.3.2 Nucleophiles

Nucleophiles are electron-rich species that donate electron pairs to electrophiles. This process typically results in the formation of a new covalent bond. Nucleophiles usually contain atoms that are either negatively charged, or, more frequently, contain lone electron pairs that are not bonded.

Molecules with a π -bond, such as ethene or benzene, can also act as nucleophiles, due to the high electron density of the π -system.

Examples of nucleophiles include H_2O , NH_3 , and OH^- .

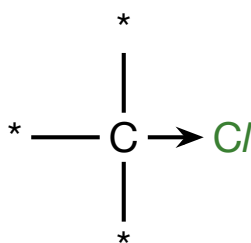
4 Induction and Resonance

4.1 Inductive Effect

The inductive effect occurs through covalent bonds, where there is a significant difference in the electronegativity of participating atoms. Electrons are either withdrawn or donated through a σ -bond, due to the polarity of the molecule.

4.1.1 Withdrawal

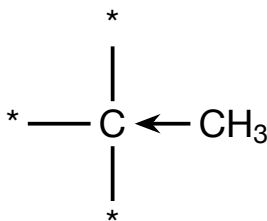
Below, Cl is more electronegative than the carbon it is bonded to. As such, it *inductively withdraws* electrons through the σ -bond.



Note that the arrow represents a withdrawal of electrons, *not* a dative bond.

4.1.2 Donation

Alkyl groups, or groups with the general formula $\text{C}_n\text{H}_{2n+1}$, *inductively donate* electrons. This behaviour is due to hyperconjugation, which lowers the total energy of the system, through an interaction between electrons in a σ -bond of the alkyl group, with a partially-filled or empty p-orbital in the adjacent atom.



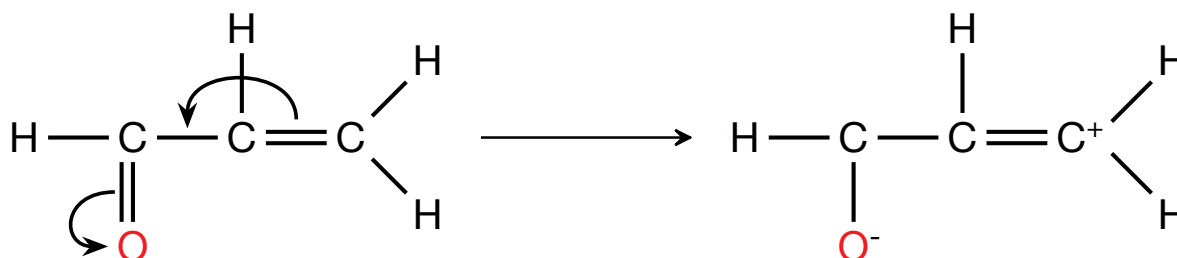
Again, the arrow *does not* represent a dative bond.

4.2 Resonance Effect

The resonance effect is the withdrawal or donation of electrons through the side-on overlap of *unhybridised* p-orbitals. Thus, the resonance effect can only occur when the substituent is bonded to an aromatic ring (π -system), or an alkene ($C=C$).

4.2.1 Withdrawal

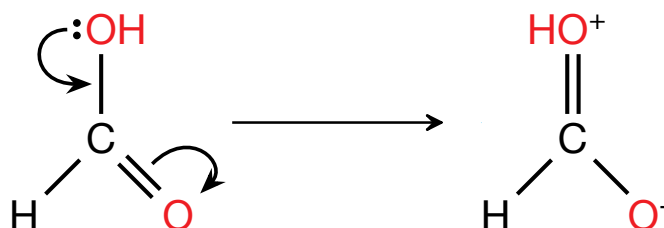
In the case below, electrons flow from the double-bonds to the substituent, via the resonance effect. In general, substituents that exhibit an electron-withdrawing resonance effect usually take the form $-Y=Z$, where Z is more electronegative than Y. Examples include carbonyls and nitriles.



Electrons move from the electron-rich double-bonds, which have unhybridised p-orbitals, to an adjacent atom.

4.2.2 Donation

On the other hand, groups can donate electrons through resonance, flowing from the substituent to a single-bond, forming a double-bond. Substituents such as halogens (F, Cl, etc.), hydroxyls ($-OH$), and amines ($-NH_2$) are examples. They usually contain a lone pair of electrons that are free for donation.



This example shows both resonant withdrawal and donation.

4.2.3 Overall Effect

Since it is possible for a substituent group to simultaneously withdraw and donate electrons through different mechanisms, it can be difficult to determine whether the overall effect serves to withdraw or donate electrons.

Behold, the second ugly table.

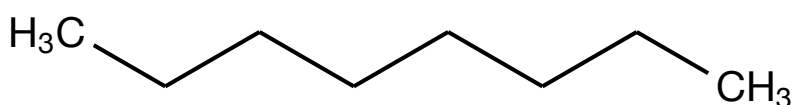
Substituent Group	Strength	Overall Effect
Alkyl groups, eg. CH_3	Weak	Donating
OH , NH_2 , OCH_3	Strong	Donating
Cl , Br	Normal	Withdrawing
CHO , NO_2 , CN , CO_2H	Strong	Withdrawing

5 Alkanes

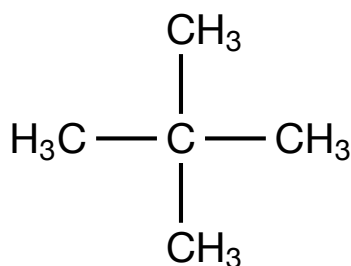
5.1 Open Chain

Open chain alkanes have the general formula of C_nH_{2n+2} . They are called 'open-chain' because the two ends of the chain are separate, in contrast with cycloalkanes.

Open chain alkanes can either be straight-chained or branch-chained. The terminology should be pretty much self explanatory.



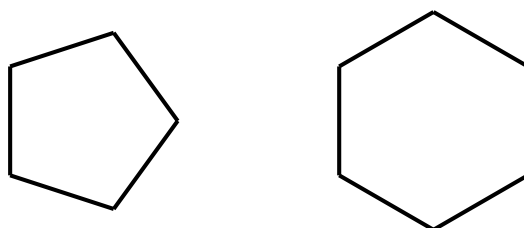
Octane is an example of a straight-chain alkane.



2,2-dimethylpropane is an example of a branched alkane.

5.2 Cycloalkanes

Cycloalkanes are alkanes where the carbon atoms at either end of the chain are bonded together, forming a closed loop. They are essentially 'closed-chain' alkanes. They take the shape of regular polygons — cyclopropane is just a triangle, and cyclobutane is a square.



Cyclopentane (left) and cyclohexane (right)

5.3 Physical Properties of Alkanes

5.3.1 Melting and Boiling Points

The melting and boiling points of alkanes follow a simple pattern. Due to the fact that they rely solely on induced dipole interactions for intermolecular bonding, both melting and boiling points increase with the length of the carbon chain, and by extension M_r . Note that small chains (eg. CH_4) have very low boiling points.

However, because branched alkanes have a smaller surface area for a given number of carbon atoms than straight-chained alkanes, their melting and boiling points will be lower, due to a smaller area for polarisation.

5.3.2 Density

Most liquid alkanes, up to a certain point, are less dense than water. Additionally, since they are insoluble, they form an immiscible layer above water.

As the number of carbon atoms increases, the strength of the intermolecular interactions will increase as well — this forces each molecule ever so slightly closer together, marginally increasing density.

5.3.3 Solubility

As described before, alkanes rely only on induced-dipole interactions for intermolecular bonding; they are insoluble in polar solvents such as water. However, they are highly soluble in non-polar solvents like CCl_4 . In fact, since solubility is dependent on the strength of solvent-solute bonds, larger alkanes will be more soluble in non-polar solvents.

5.4 Free Radical Substitution of Alkanes

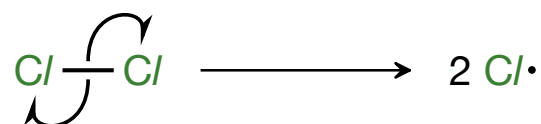
5.4.1 Mechanism of Reaction

In the steps below, the free radical substitution of methane [CH₄] by chlorine [Cl₂] will be used. This applies for any alkane, and a sufficiently reactive halogen (Usually either Cl or Br).

The observable change would be a decolourising of the halogen gas, as it is consumed. This is *reddish-brown* for bromine, and *yellowish-green* for chlorine. Conditions for the reaction simply include the alkane and gaseous halogen gas, as well as UV light.

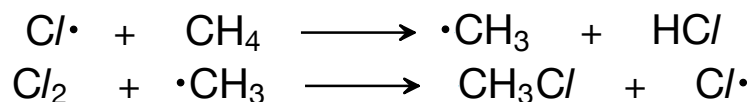
Stage I Initiation

The Cl–Cl bond is *homolytically* broken to form 2 Cl• radicals. The energy required to break this bond is provided by the UV light.



Stage II Propagation

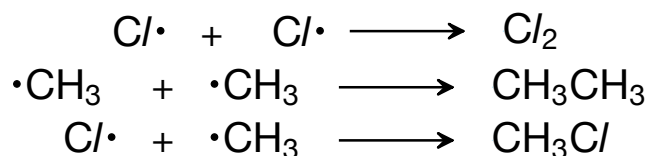
The highly reactive Cl• radicals then react with the CH₄ molecules, bonding with one of the hydrogen atoms to form HCl and a carbocation radical, CH₃•.



This newly-minted CH₃• radical can react with a Cl₂ molecule to form CH₃Cl and another Cl• radical, thus recreating the consumed radical. As long as the supply of Cl₂ gas has not been exhausted, this reaction can continue, and no additional UV light is required to sustain it.

Stage II Termination

In the termination stage, two radicals combine to form stable products, effectively terminating the chain reaction.

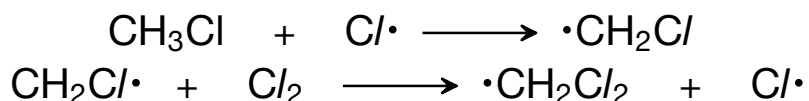


Once all the radicals have been consumed in this manner, the reaction will stop, unless more UV light is provided (along with more Cl_2 gas).

5.4.2 Multi-substitution of Alkanes

Free radical substitution of alkanes is usually not the preferred way to produce halogenoalkanes, due to the random nature of the process and the possibility of multi-substitution, where more than one halogen atom has been substituted onto the alkane.

If there are still $\text{Cl}\cdot$ radicals remaining, in the reaction chamber, CH_3Cl formed during the termination stage can still react with it, forming a $\text{CH}_2\text{Cl}\cdot$ radical, which can continue to react.



Indeed, this can continue *ad-infinitum*, so until all the hydrogen atoms on the alkane have been substituted. In the case of methane, this results in the formation of CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 .

In fact, there will also be a small amount of alkanes with more than 1 carbon in the chain; this is due to the possibility of two molecules of $\cdot\text{CH}_2\text{Cl}$ reacting, which then has its hydrogens further substituted.

6 Alkenes

7 Arenes

8 Halogen Derivatives