Organic Chemistry

$C_8H_{10}N_4O_2$
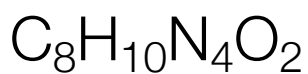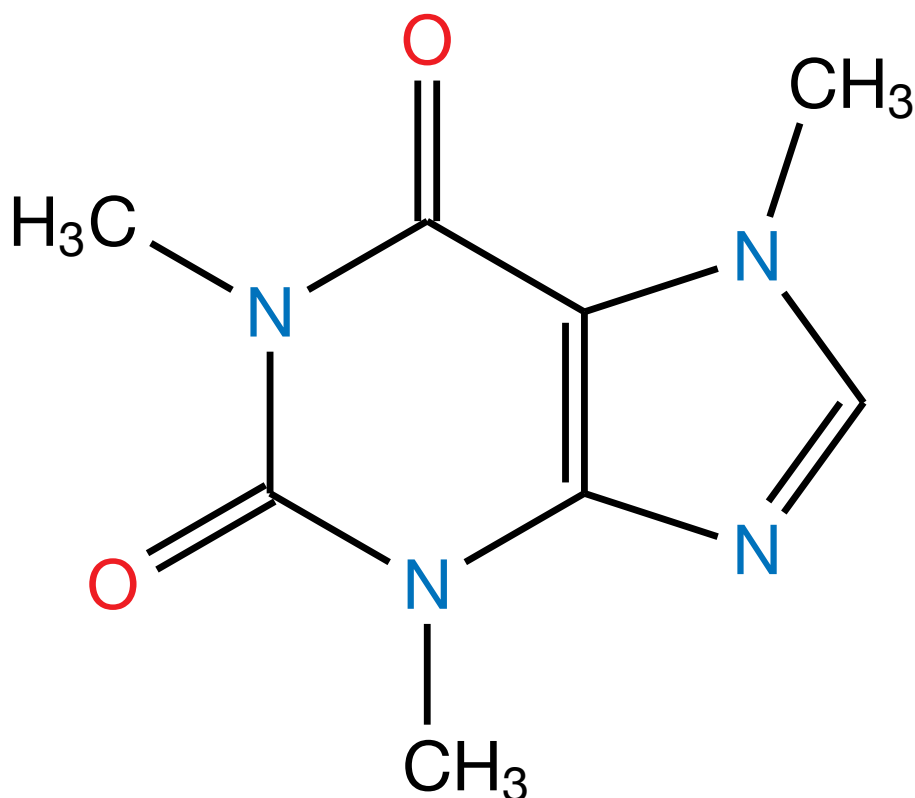
1,3,7-trimethylpurine-2,6-dione

-

Caffeine

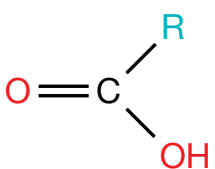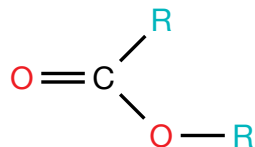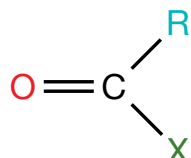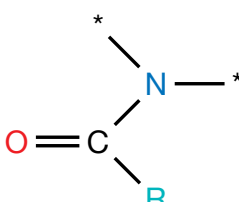Chapters 8 to 12

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.

R, as used below, represents a substituent alkyl or aryl group, the former being an arbitrary carbon chain, and the latter being some aromatic ring derivative.

Name	Prefix Form	Suffix Form	Structure
Carboxylic Acid	carboxy–*	*–oic acid	
Ester	–	*–oate	
Acyl Halide	halocarbonyl–*	*–oyl halide	
Amide	carbamoyl–*	*–amide	

|			
Nitrile	cyano–*	*–nitrile	N≡C—R
Aldehyde	formyl–*	*–al	O=C(R)(H)
Ketone	oxo–*	*–one	O=C(R)(R)
Alcohol	hydroxy–*	*–ol	*—C(*)(*)—OH
Amine	amino–*	*–amine	R—N(*)(*)
Alkene	alkenyl–*	*–ene	*₂C=C*₂
Ether	alkoxy–*	–	R—O—R
Alkyl Halide	halogen–*	–	*—C(*)(*)—X

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 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 id-id interactions).
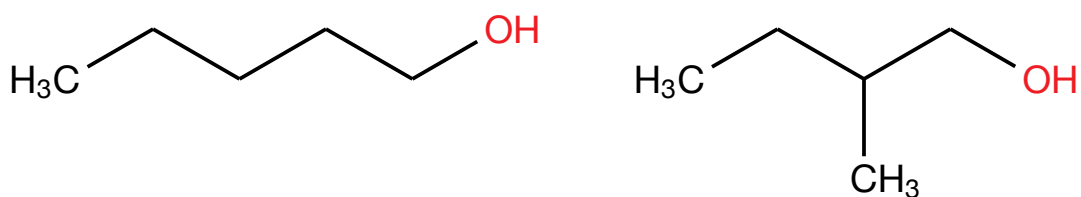
Pentanol and 3-methylbutan-1-ol are chain isomers.

2.2.2   Positional Isomerism

Positional isomers have the same arrangement their of carbon chains, and the same functional groups. However, said functional groups are placed at different positions.
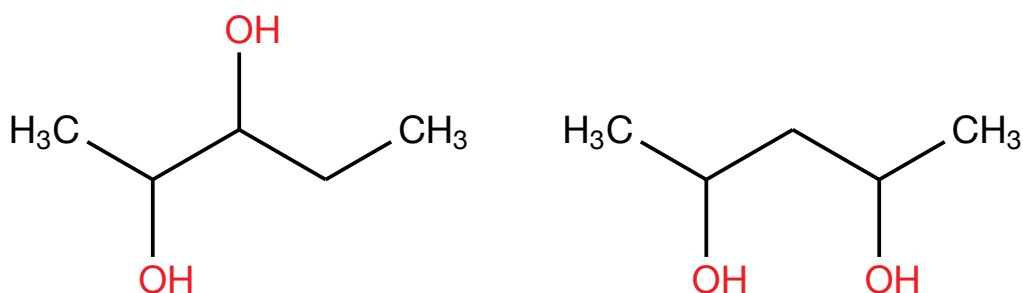
Butan-2,3-ol and butan-2,4-ol are positional isomers.

2.2.3 Functional Group Isomerism

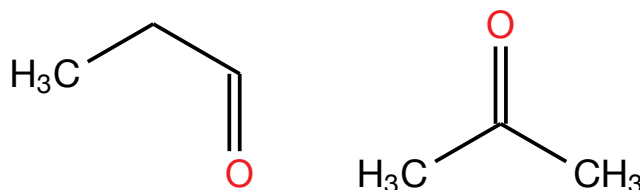This is somewhat a misnomer, since it is exactly the opposite of what it seems to intuit. Functional group isomers share only their molecular formulas; the carbon chain, the functional groups, etc. are all different.

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 isomersim.

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.
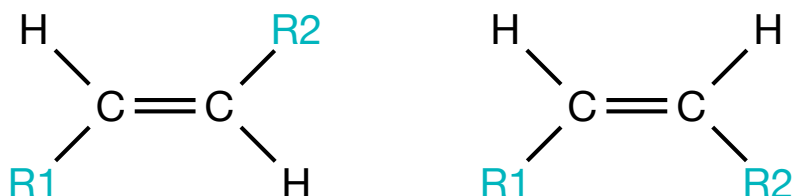

The molecule on the left is the *trans* isomer, while the one on the right is the *cis* isomer. *trans* is from Latin, meaning *other side*, while *cis* obviously means *same side*. In the former, the larger groups are on opposite sides of the alkene double bond, while in the latter, the larger groups 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.
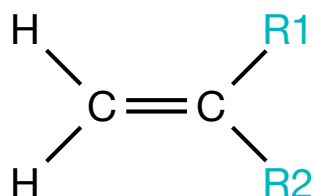
2.3.3 E/Z Isomerism

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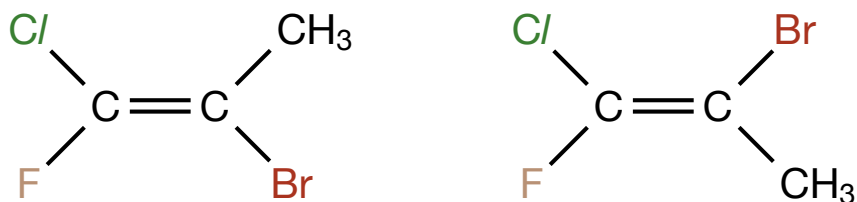
It has 4 distinct substituents, and thus a cis/trans designation cannot be used. Behold, E/Z isomerism. At its core it is simply another method of handling alkene isomers that works for more general forms of molecules.

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.
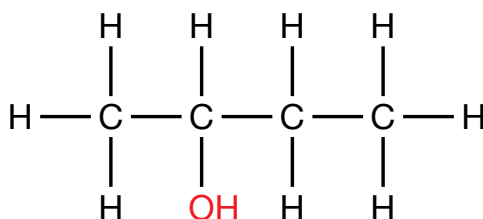
Indeed, it can take the form of 2 non-superimposable mirror images, that are differentiated by the adjacency of 2 of the 4 groups bonded to the chiral carbon. As can be seen, these two mirror images cannot be rearranged into the other, and are distinct — these are called *enantiomers*.
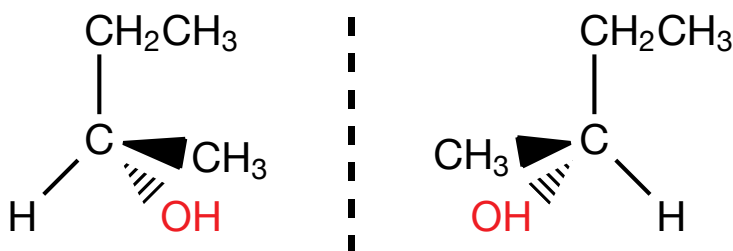
The solid wedge indicates a bond coming out of the plane of the paper, while the dashed wedge indicates a bond going into the plane.

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.
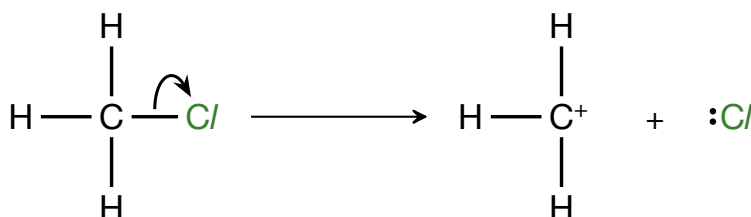
The movement of these single electrons is represented with single-hooked arrows. The arrow starts from the bond line, and points towards the target atom receiving the electron.
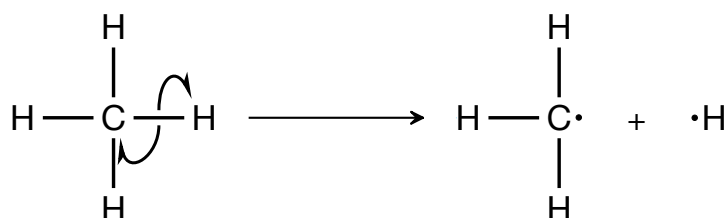
The homolytic fission of CH_4, forming $\cdot CH_3$ and $\cdot H$ radicals.

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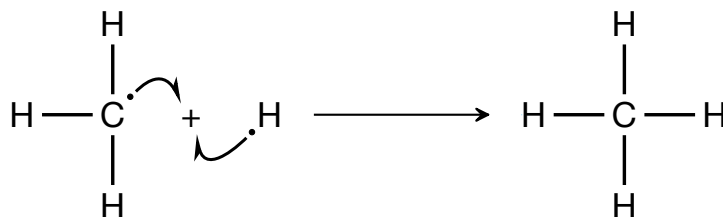
The formation of a bond between ·CH_3 and ·H radicals to form CH_4.

3.2.2 Electron Pairs

Electron pairs usually come from negatively charged radicals or lone pars, 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.
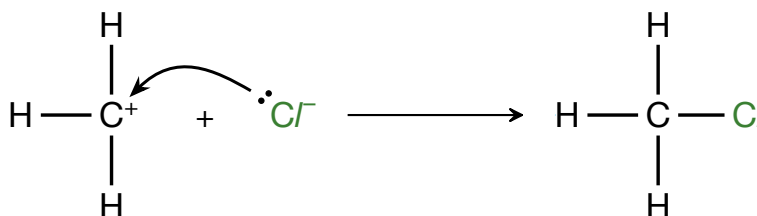
The formation of a bond between ·CH_3 and Cl^- radicals, to form CH_3Cl.

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.
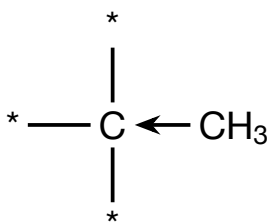
4.1.1 Withdrawal

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

$$
\begin{array}{c}
* \\
| \\
* \!-\! C \!\longrightarrow\! Cl \\
| \\
*
\end{array}
$$
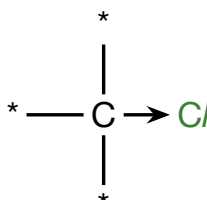
Note that the arrow represents a withdrawal of electrons, *not* a dative bond.

4.1.2 Donation

Alkyl groups, or groups with the general formula C_nH_{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.

$$
\begin{array}{c}
* \\
| \\
* \!-\! C \!\longleftarrow\! CH_3 \\
| \\
*
\end{array}
$$

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).
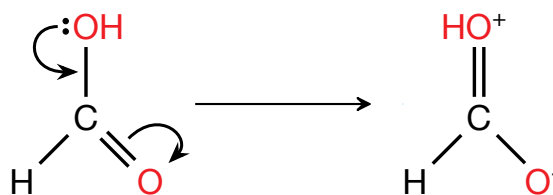
4.2.1   Withdrawal

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 of –Y=Z, where Z is more electronegative than Y. Examples include carbonyls and nitriles.
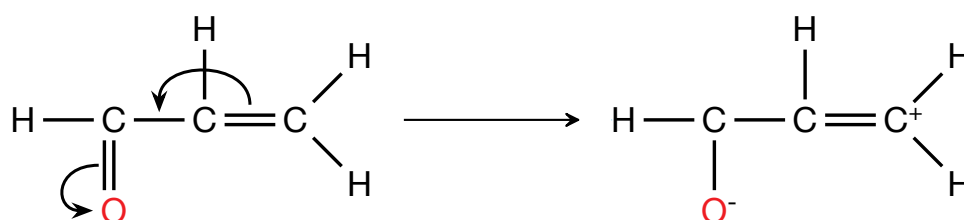
Electrons move from the electron-rich double-bonds, which have unhybridised p-orbitals, to an adjacent atom.

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, C*l*, 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 endsof 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.
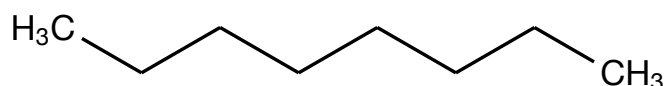

Octane is an example of a straight-chain alkane.
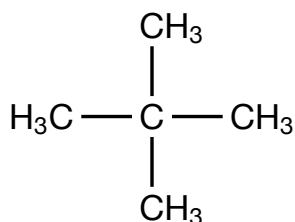
2,2-dimethylpropane is an example of a branched alkane.

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.
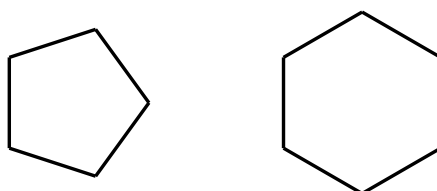
Cyclopentane (left) and cyclohexane (right)

5.3   Physical Properties

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 (CH_4) by chlorine (Cl_2) will be used. This applies for any alkane, and a sufficiently reactive halogen.

Conditions: UV Light, Br_2 / Cl_2 gas
**Observations:**   *reddish-brown* Br_2 / *yellowish-green* Cl_2 decolourises.

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.

$$Cl-Cl \longrightarrow 2\ Cl\cdot$$
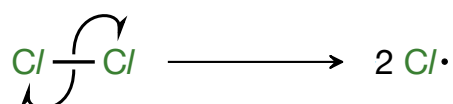
Stage II   Propagation
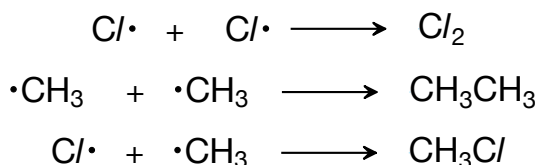
The highly reactive Cl radicals then react with the CH_4 molecules, bonding with one of the hydrogen atoms to form HCl and a carbocation radical, CH_3.

$$Cl\cdot\ +\ CH_4 \longrightarrow \cdot CH_3\ +\ HCl$$
$$Cl_2\ +\ \cdot CH_3 \longrightarrow CH_3Cl\ +\ Cl\cdot$$
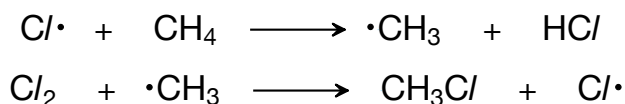
This newly-minted CH_3 radical can react with a Cl_2 molecule to form CH_3Cl and another Cl radical, thus recreating the consumed radical. As long as the supply of Cl_2 gas has not been exhausted, this reaction can continue, and no additional UV light is required to sustain it.

Stage II   Termination

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

$$Cl\cdot \; + \; Cl\cdot \longrightarrow \; Cl_2$$

$$\cdot CH_3 \; + \; \cdot CH_3 \longrightarrow \; CH_3CH_3$$

$$Cl\cdot \; + \; \cdot CH_3 \longrightarrow \; CH_3Cl$$

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 halogenated alkanes, 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 Cl radicals remaining, in the reaction chamber, CH_3Cl formed during the termination stage can still react with it, forming a CH_2Cl radical, which can continue to react.

$$CH_3Cl \; + \; Cl\cdot \longrightarrow \; \cdot CH_2Cl$$
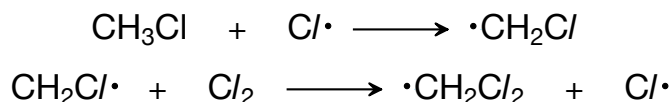
$$CH_2Cl\cdot \; + \; Cl_2 \longrightarrow \; \cdot CH_2Cl_2 \; + \; Cl\cdot$$

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, the 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 $\cdot CH_2Cl$ reacting, which then has its hydrogens further substituted.

5.4.3   Isomerism of Substituted Alkanes

Because every hydrogen atom can be substituted by the halogen atom, alkanes with 3 or more carbon atoms in the chain can form isomers. The probability of the formation of each isomer depends on both the number of possible hydrogen atoms that can be substituted to result in it, as well as the stability of the carbon radical intermediate.
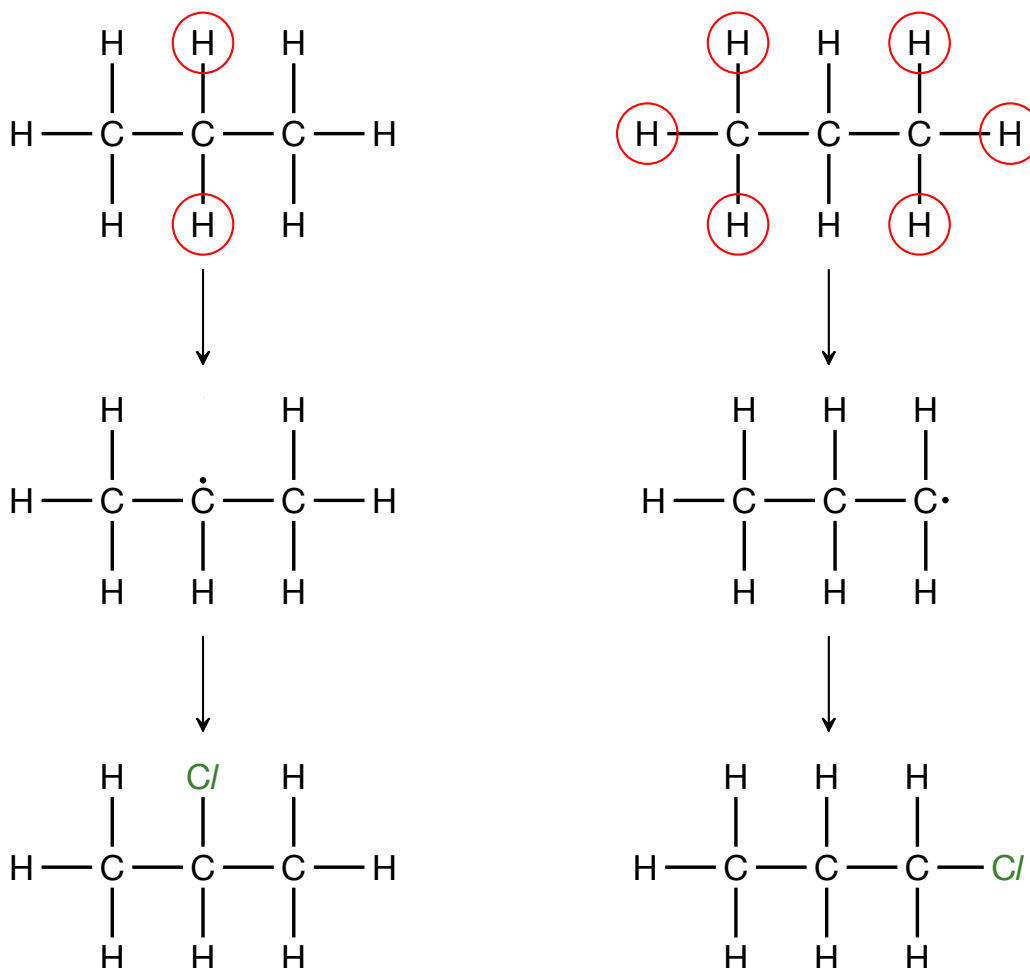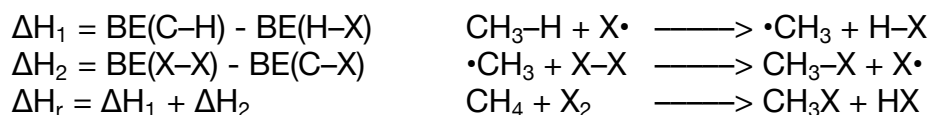

In the example above, propane can be substituted by Cl to form 2 different isomers, 2-chloropropane and 1-chloropropane. Only 2 hydrogens can be substituted to form the former, while 6 hydrogens can be substituted to form the latter. Thus, the *expected* ratio of products from the free radical substitution of propane with chlorine is 2 : 6 in favour of 1-chloromethane.

However, the stability of the carbon radical intermediate also plays a part in the ratio of products. For 1-chloropropane, it involves forming a carbon radical on carbon 1, which only has 1 electron-donating alkyl group (through the induction effect) to stabilise the positive charge. On the other hand, for 2-chloropropane, the positive charge is on carbon 2, which has 2 electron-donating alkyl groups to stabilise it. Thus, it is more likely to form, and hence 2-chloropropane is more likely to form. Therefore, the actual ratio of products is around 4 : 6, not 2 : 6.

5.4.4 Free Radical Substitution Reactivity

The reactivity of the free radical substitution naturally depends on the species of halogen that is reacting. As is typical of halogens, the reactivity increases in this order: $I_2 < Br_2 < Cl_2 < F_2$. In fact, the substitution by fluorine is too reactive — even in the dark and at room temperature. On the other hand, the substitution of iodine is not feasible ($\Delta G > 0$).

In the propagation steps of the reaction, several bonds are formed and broken. Using X as a halogen atom:

$\Delta H_1 = BE(C–H) - BE(H–X)$ $CH_3–H + X• \longrightarrow •CH_3 + H–X$
$\Delta H_2 = BE(X–X) - BE(C–X)$ $•CH_3 + X–X \longrightarrow CH_3–X + X•$
$\Delta H_r = \Delta H_1 + \Delta H_2$ $CH_4 + X_2 \longrightarrow CH_3X + HX$

The values of the bond energies for H–X, X–X, and C–X are below:

F_2	H–F	$= 562\,kJ\,mol^{-1}$
	C–F	$= 484\,kJ\,mol^{-1}$
	F–F	$= 158\,kJ\,mol^{-1}$
	ΔH_r	$= -478\,kJ\,mol^{-1}$
Cl_2	H–Cl	$= 431\,kJ\,mol^{-1}$
	C–Cl	$= 340\,kJ\,mol^{-1}$
	Cl–Cl$_2$	$= 244\,kJ\,mol^{-1}$
	ΔH_r	$= -117\,kJ\,mol^{-1}$
Br_2	H–Br	$= 366\,kJ\,mol^{-1}$
	C–Br	$= 280\,kJ\,mol^{-1}$
	Br–Br	$= 193\,kJ\,mol^{-1}$
	ΔH_r	$= -43\,kJ\,mol^{-1}$
I_2	H–I	$= 299\,kJ\,mol^{-1}$
	C–I	$= 240\,kJ\,mol^{-1}$
	I–I	$= 151\,kJ\,mol^{-1}$
	ΔH_r	$= +22\,kJ\,mol^{-1}$

As can be seen, the reaction with F_2 is highly exothermic; even the F–F bond energy is relatively small, hence the reaction is highly spontaneous — even at room temperature and without UV light, since the initiation stage requires little energy to progress.

On the other hand, the ΔH of the reaction with I_2 is positive, hence the reaction is not as spontaneous, and it is not as likely to take place.

5.5 Classification of Atoms with Substituents

This applies to many things — carbons, halogenoalkanes, and alcohols. Essentially, the classification of an atom with substituent groups refers to the number of such groups attached to the carbon, and the number of hydrogens (ie. unfilled slots so to speak) attached to it.

As example, there are 4 possible classifications of carbons in an alkane: *primary*, *secondary*, *tertiary*, and *quaternary*.

$H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - R1$	$H - \underset{\underset{H}{|}}{\overset{\overset{R2}{|}}{C}} - R1$	$R3 - \underset{\underset{H}{|}}{\overset{\overset{R2}{|}}{C}} - R1$	$R3 - \underset{\underset{R4}{|}}{\overset{\overset{R2}{|}}{C}} - R1$
Primary (1°)	Secondary (2°)	Tertiary (3°)	Quaternary (4°)

The table (ew) above gives a visual representation. *R* represents an alkyl group substituent. This principle also applies when classifying alkyl radicals.

5.6 Combustion of Alkanes

Alkanes are a type of combustible fuel, and there exists a general formula describing the required amounts of O_2 to combust a given hydrocarbon.

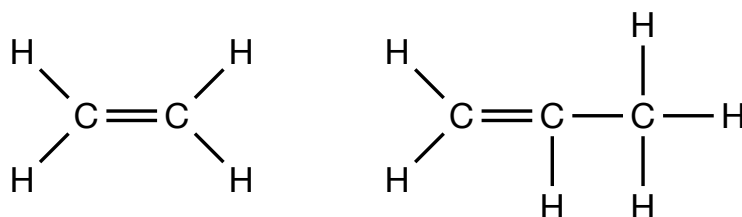$$C_xH_y \quad + \quad x + \tfrac{y}{4}O_2 \quad \longrightarrow \quad xCO_2 \quad + \quad \tfrac{y}{2}H_2O$$
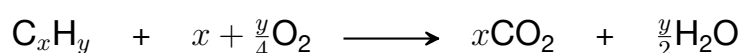
Note that while this combustion process is highly exothermic, it still has a high activation energy, and requires an energy input like a spark to begin the reaction.
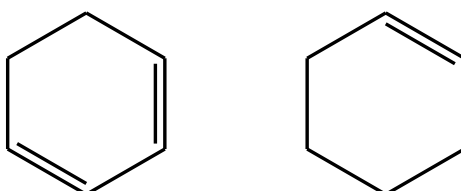
6   Alkenes

6.1   Open Chain

Alkenes are simply unsaturated hydrocarbons, with one or more double bonds. They have the general form of C_nH_{2n}

Ethene (C_2H_4) and propene (C_3H_6) are examples of alkenes.

6.2   Cycloalkenes

Cycloalkenes are simply cycloalkanes where one or more of the $C-C$ bonds have been replaced with a $C=C$ double bond.

Cyclohex-1,3-ene and cyclohexene are examples of cycloalkenes.

6.3   Physical Properties

The physical properties of alkenes, including melting and boiling points, density and solubility follow the same trends as alkanes. Larger molecules have higher melting and boiling points, and higher densities, and alkenes are generally only soluble in non-polar solvents.

6.4   Stability of Carbocations

Before reactions and mechanisms of alkenes can be discussed, it is important to note the rules governing the formation of products, and the behaviour of molecules during the reaction.

All physical systems have a tendency to move to the lowest energy state — this state is characterised by the formation of the most stable molecules. As such, ions and radicals are inherently unstable.

6.4.1   Structure

One of the important intermediate products are carbocations, which are alkyl groups with an sp^2 hybridised central carbon atom, and carries a positive charge on that atom.
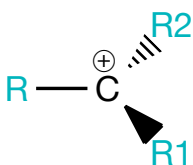
The 3 substituent groups are arranged in a trigonal planar fashion, with the p-orbitals above and below this plane. As such, nucleophiles can attack the carbocation from either the top or bottom.

6.4.2   Stability

Charged ions are inherently more unstable than their neutral molecule counterparts; any species that stabilises the charge on the carbon ion would in turn increase the stability of the entire molecule. The primary reason for this is that molecules that are created from a more stable intermediate product have a higher chance to form. Thus, the probability of formation of a given product of a reaction can be estimated by looking at the stability of the intermediate compound leading to its creation.

For carbocations, the carbon atom has a positive charge, thus electron-donating substituents such as alkyl groups ($-CH_3$), would stabilise the ion, as the donated electrons partially disperse the positive charge on the central atom.

Conversely, electron-withdrawing species such as halogens (F_2, Cl_2 etc.) would further destabilise the carbocation, and as such products that involve the formation of these intermediates would have constitute much lower proportion of the final products.

6.5 Electrophilic Addition

The primary reaction mechanism of alkenes is electrophilic addition. Due to the high electron density of the π-bonds, electrophiles are readily attracted — thus alkenes are far more reactive than alkanes.

During a reaction, the comparatively weaker π-bond is preferentially broken over the stronger σ-bond; only a C−C bond remains, and atoms are *added* to the carbons, since they are now able to form an additional bond each. Hence, electrophilic *addition*.

6.5.1 Electrophilic Addition of Hydrogen Halides

In this reaction, the hydrogen and halogen atom are added across the double bond of the alkene. The hydrogen halide should be in a gaseous state for this reaction.

Conditions: Gaseous HX (usually HC*l* or HBr).

Step 1
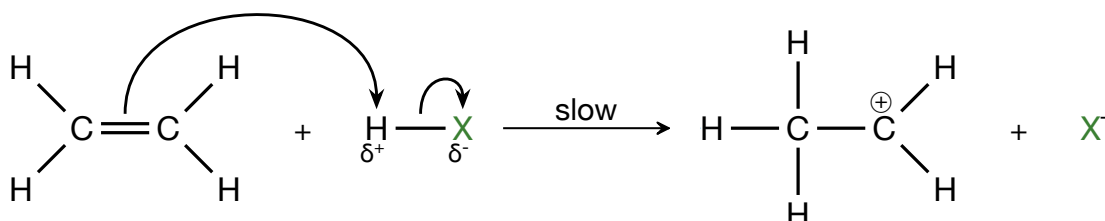
This is the rate-determining step, which involves the breaking of the π-bond. The polar HX molecule has to approach the electron cloud of the π-bond in the correct orientation (hydrogen-facing), where the π-bond electrons attack the electron deficient, $\overset{\delta+}{H}$ atom.

The H−X bond then undergoes heterolytic fission, producing a carbocation intermediate and a halide ion.

Step 2
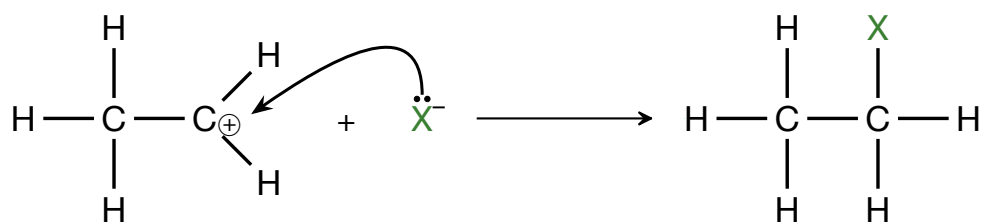
Note that the electron pair arrow points to the plus charge on the carbon, *not* the carbon atom itself.

This is the fast step; the bromide anion acts as a nucleophile, attacking the positively-charged carbocation. Since this step involves the reaction of two oppositely-charged species, it is a fast step.

## Overall Reaction
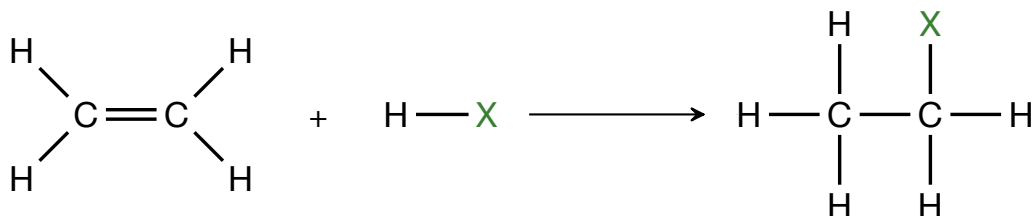
6.5.2 Markovnikov's Rule

This rule governs the major product that is formed when asymmetrical compounds are electrophilically added to alkenes, such as hydrogen halides. It does not apply to symmetrical reactants like Cl_2 or Br_2.

The rule states basically states that when a hydrogen compound with the general form H−X is added to an alkene that is asymmetrical about the double-bond, the hydrogen atom will be added to the carbon with *more* existing hydrogen atoms. Note that X can be a halogen, a hydroxide (ie. H−X is H_2O) or some other electronegative species.

6.5.3 Addition of H–X to Unsymmetrical Alkenes

The behaviour that Markovnikov's rule predicts can be derived from the fact that adding the non-hydrogen species to the least substituted carbon would result in a less stable intermediate being formed. This can be illustrated using the electrophilic addition of HBr to prop-1-ene (C_3H_6).

If the Markovnikov's rule is *not* followed, the following will take place:
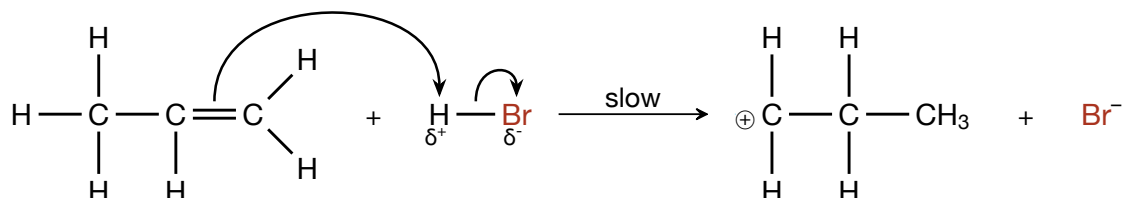
The hydrogen was added to the centre carbon, in violation of Markovnikov's rule.

Notice that the positively-charged carbon on the intermediate only has 1 electron-donating alkyl group to stabilise its charge. Conversely, if Markovnikov's rule is followed below, the outcome would be different.
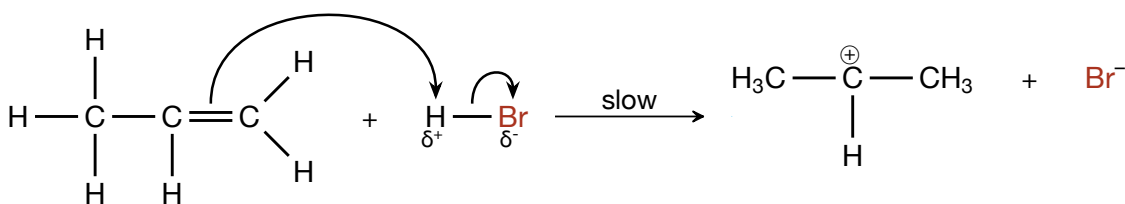
The hydrogen was added to the terminal carbon, following Markovnikov's rule.

In this case, the carbon atom containing the positive charge has 2 electron-donating alkyl groups attached to it, making this intermediate molecule more stable than the one above it.

As such, it is more likely to form, and hence 2-bromopropane will be the *major product*, and 1-bromopropane will be the *minor product*.

6.5.4 Electrophilic Addition of Halogens

The electrophilic addition of halogens to alkanes does not involve Markovnikov's rule, since it is symmetrical. As the non-polar halogen molecule approaches the high-electron-density π-bond, it is polarised, forming δ⁺ and δ⁻ partial charges.

Note that the halogens used are usually either Br_2 or Cl_2, since F_2 is too reactive, and I_2 is too *unreactive*. The reaction mechanism involves the formation of a *cyclic halonium ion* (bromonium or chloronium) — the double bond breaks, and each carbon forms a single bond with one positive halide ion (both carbons bond to the same atom).

Conditions: No UV Light, gaseous X_2.
**Observations:**   *reddish-brown* Br_2 / *yellowish-green* Cl_2 decolourises.

Step 1

This initial step is the slow, rate-determining one. It involves breaking of the π-bond, as well as the X−X bond. Note that the resulting cyclic halonium ion is highly unstable, due to the inherent strain of having a three-membered ring.
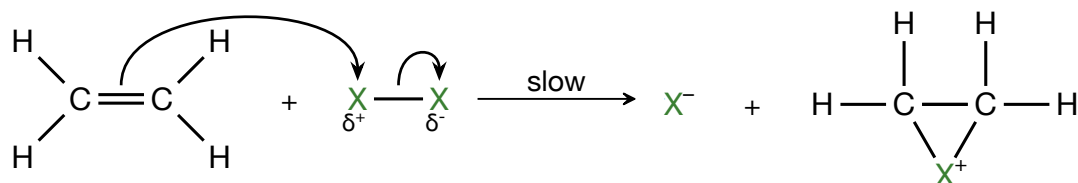

Step 2

In the second, fast step, the negatively-charged bromide ion from the first step attacks the overall positively-charged cyclic bromonium ion, resulting in the final product. Note that the bromide ion attacks one of the carbons attached to the positive bromide ion, breaking that bond. This is the fast step as it involves the reaction of two oppositely-charged species.
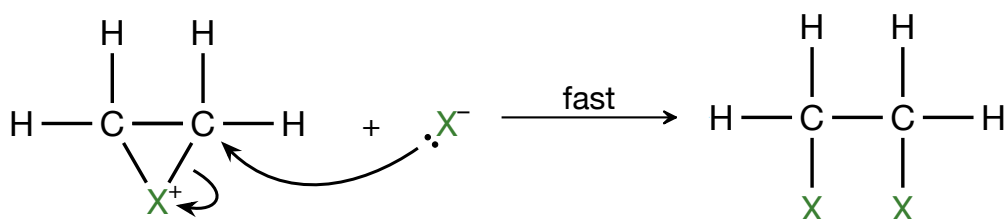
Overall Reaction
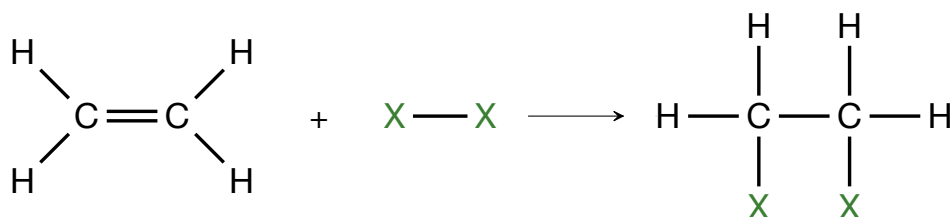
6.5.5 Electrophilic Addition of Aqueous Br$_2$

The mechanics of this reaction are basically the same as that of the electrophilic addition of Br$_2$. The conditions and observations are fairly similar as well, except for the colour change — aqueous Br$_2$ is *yellow*, not reddish-brown.

Also, since the Br atoms are not both added across the double bond in a symmetrical manner, Markovnikov's Rule applies — the OH group will preferentially attack the carbon that has more stabilising alkyl groups.

Conditions: No UV Light, aqueous Br$_2$.
Observations: *yellow* Br$_{2(aq)}$ decolourises.

Step 1
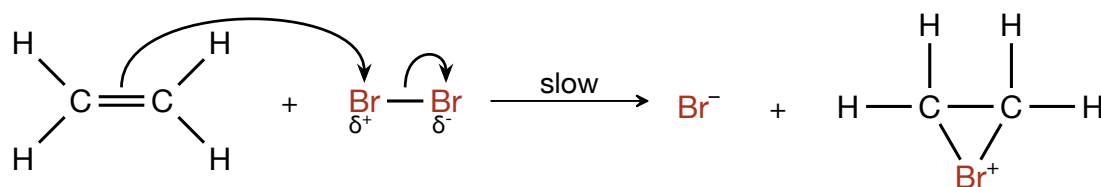
The cyclic bromonium ion is formed.

Step 2

Once the cyclic bromonium ion is formed however, it is susceptible to attack from any and all nucleophiles — including water, which has lone pairs and is a stronger nucleophile Br$^-$. Since it is in much higher concentrations than Br$^-$, the primary product will now have an OH group.
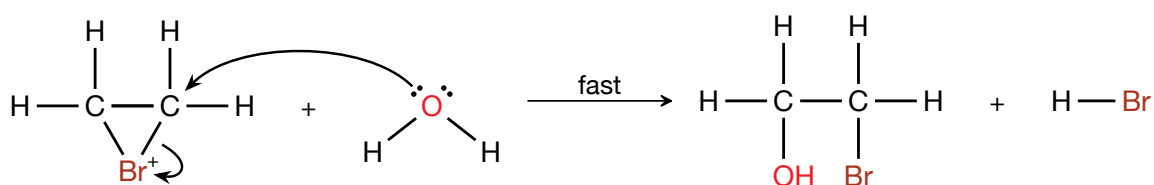
Overall Reaction
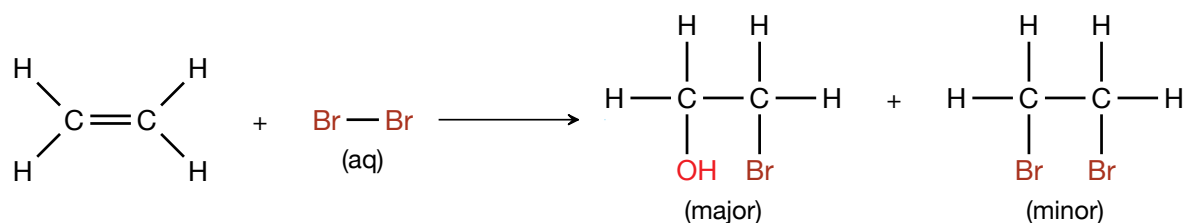
Both products are formed, except 1,2-dibromoethane is in much lower proportions.

6.5.6 Electrophilic Addition of Steam (Hydration)

Under certain (usually industrial) conditions, alkenes can react with steam to form alcohols. Since this reaction involves the formation of a carbocation intermediate, the proportion of products will be governed by Markovnikov's Rule.

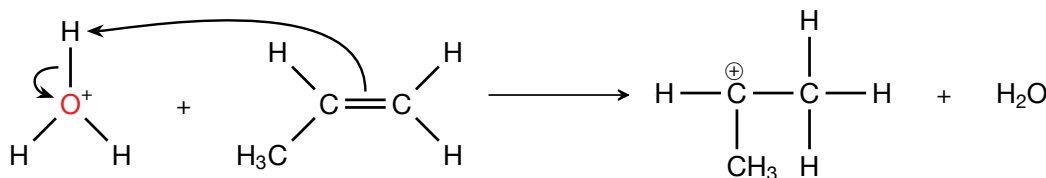**Conditions:**   300 °C, at 70 atm, H_3PO_4 catalyst.

Step 0

The first step is to form $H_3O^+_{(aq)}$. Simply put, it is aqueous H^+.
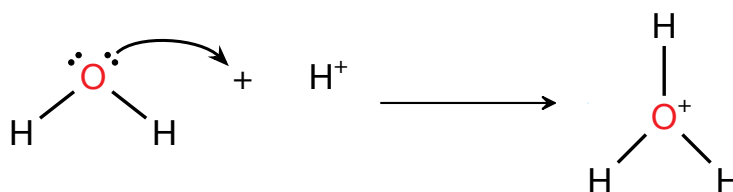
Step 1

The electron-rich double-bond (C=C) is then attacked by one of the H atoms on the H_3O^+, acting as an electrophile.

Since the alkene is not symmetrical, there are two product possibilities; hence, the positive charge will be on the carbon atom with more electron donating alkyl groups, in this case carbon 2.

Step 2

One of the lone pairs on the oxygen atom of a water molecule acts as an nucleophile, attacking the newly-formed carbocation. This results in a protonated alcohol, which is basically an alcohol with an extra H atom on the OH group.
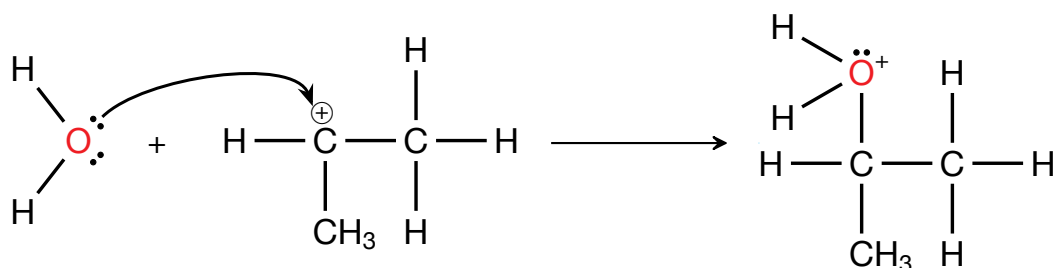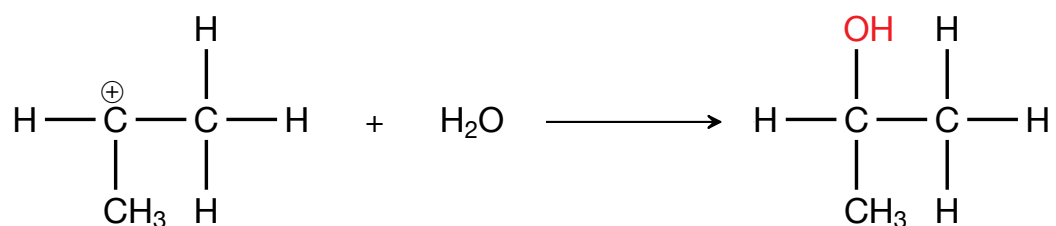
Step 3

The acid catalyst is regenerated as a lone pair on another water molecule's O atom attacks the extra H of the OH group. This forms the alcohol proper, and the H_3O^+ ion.
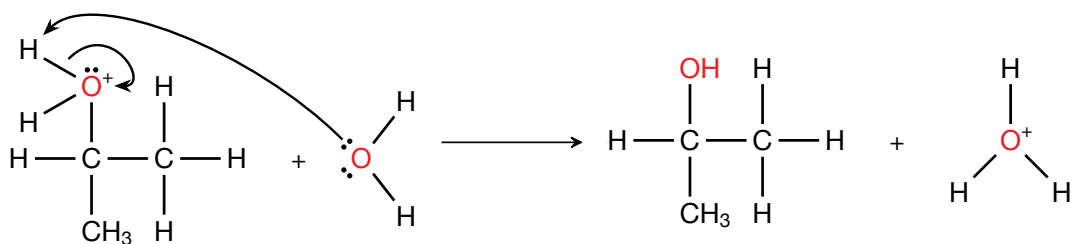
Overall Reaction

6.6 Hydrogenation of Alkenes

Hydrogen gas can be used to saturate alkenes, through the use of an insoluble metal catalyst such as nickel, palladium or platinum, as well as sufficiently high temperatures and pressures.

It was commonly used in the food industry to produce margarine from unsaturated plant oils. However, the resulting dense fats were found to be hazardous to human health, and subsequent usage was discontinued.
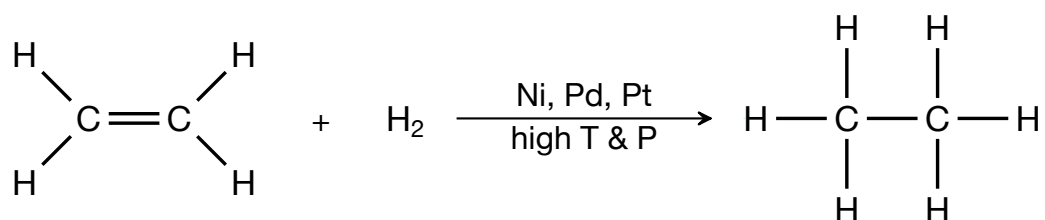
6.7 Mild Oxidation of Alkenes

Alkenes can be mildly oxidised with potassium manganate (VII), KMnO4, forming *diols*. This requires a cold environment, and either an acidic or alkaline medium (for MnO_4^- to function).

On a side note, balancing redox reactions involving organic molecules simply involves adding H_2O to balance the H or O (for oxidation and reduction respectively), and adding an appropriate number of [O] or [H] to balance the remaining oxygen or water.

6.7.1 Acidic Medium

A dilute acid is used to provide the acidic medium, in the form of H^+ ions. Typically, this is H_2SO_4. The oxidising agent, MnO_4^-, is reduced, forming Mn_2^+.
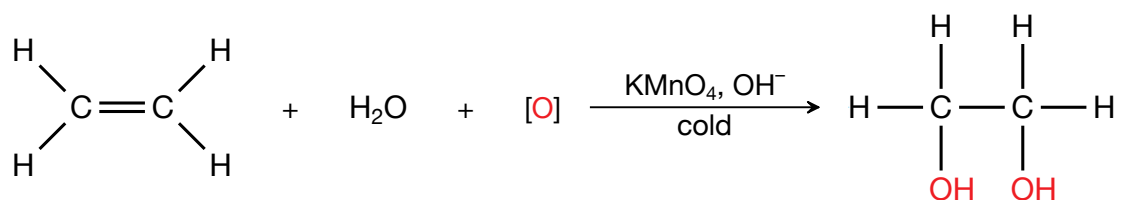
Conditions: Cold KMnO$_4$, acid (H$_2$SO$_4$).
Observations: Purple KMnO$_4$ decolourises.
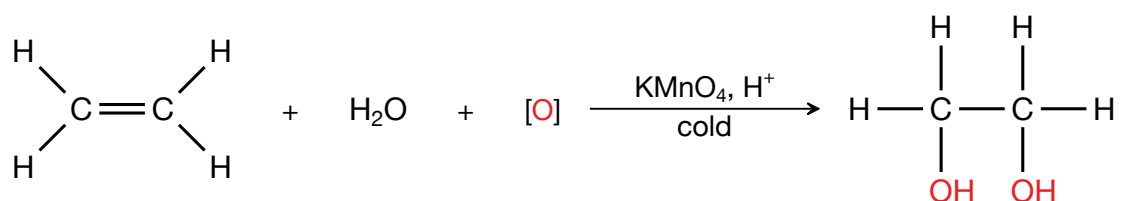
6.7.2 Alkaline Medium

An aqueous base, such as NaOH, is used to provide the OH^- ions. The oxidising agent MnO_4^- is reduced to MnO_2.

Conditions: Cold KMnO$_4$, aqueous base (NaOH).
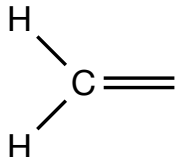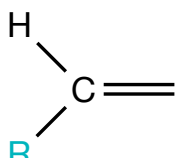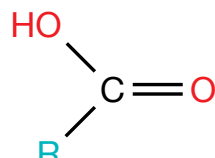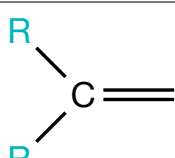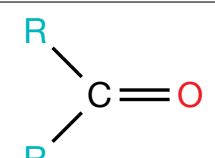**Observations:**   Purple KMnO$_4$ decolourises, forming a brown precipitate of MnO$_2$

6.8   Oxidative Cleavage (Strong Oxidation) of Alkenes

When the $KMnO_4$ solution containing an alkene is heated, *strong oxidation* will take place. The double bond is *cleaved* instead of added to, and each side of the double bond forms its own fragment. In the case of cycloalkenes however, the end product might still only be one molecule.

Furthermore, only a strong oxidising agent like MnO_4^- can be used. The difference between mild and strong oxidation also depends *only* on the temperature of the reacting solution. Only heated solutions will result in oxidative cleavage.

Depending on the number of substituents (or inversely, the number of hydrogen atoms) attached to the carbon with the double bond, there are 3 possible products. Again, a table is the best way to present this, unfortunately.

Substituents	Structure	Product
0	H, H $C=$	$CO_2 + H_2O$
1	H, R $C=$	HO, R $C=O$
2	R, R $C=$	R, R $C=O$

6.8.1   Further Oxidation of Ethanedioic Acid

The sole special case that must be noted is that if the oxidative cleavage results in the formation of ethanedioic acid ($C_2H_2O_4$), it is further oxidised to form $2\,CO_2$ and H_2O.

$$\text{HO—C(=O)—C(=O)—OH} \longrightarrow 2\,CO_2 + H_2O$$
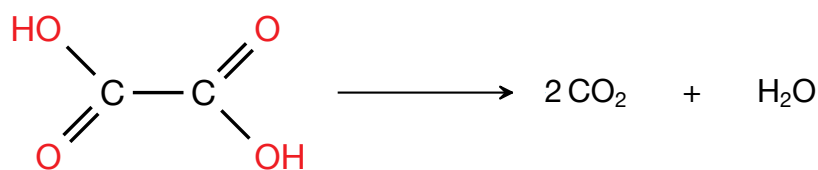
Ethandioic acid, or oxalic acid.

6.8.2 Uses of Oxidative Cleavage

Oxidative cleavage can be used to determine the position of the double bond in carbon chains and cycloalkenes, given the products (fragments) of the cleavage reaction.

Most importantly, if CO_2 is one of the products (gas evolved), then there are 2 possibilities — either the original molecule has a terminal C=C double bond, or the cleavage involved the formation of ethanedioic acid that further decomposed to form CO_2.

7   Arenes

8 Halogen Derivatives