

H2 ORGANIC CHEMISTRY: ALKENES

Lecture Outline

- 1 Introduction
- 2 Physical Properties of Alkenes
- 3 Preparation of Alkenes
 - 3.1 Dehydration of Alcohols
 - 3.2 Dehydrohalogenation of Halogenoalkanes
- 4 Reactions of Alkenes
 - 4.1 Electrophilic Addition
 - 4.11 Addition of hydrogen halides
 - 4.12 Addition of halogens in CCl₄
 - 4.13 Addition of halogens in water
 - 4.14 Addition of water
 - 4.2 Reduction
 - 4.3 Oxidation
 - 4.31 Combustion
 - 4.32 Formation of diol (mild oxidation)
 - 4.33 Formation of carboxylic acids, ketones and/or CO₂ (strong oxidation)
- 5 Tests for Alkenes
- 6 Summary

Assessment Objectives

Candidates should be able to:

- (a) explain the general reactivity of alkenes towards electrophilic reagents/electrophiles
- (b) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
 - (i) electrophilic addition of water/steam, hydrogen halides and halogens
 - (ii) reduction via catalytic hydrogenation (catalytic addition of hydrogen)
 - (iii) oxidation by cold, alkaline solution of manganate(VII) ions to form the diol
 - (iv) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon–to–carbon double bond in order to determine the position of alkene linkages in larger molecules
- (c) describe the mechanism of electrophilic addition in alkenes, using bromine with ethene as an example
- (d) apply Markovnikov's rule to the addition of hydrogen halides to unsymmetrical alkenes, and explain the composition of products in terms of the stability of carbocation intermediates

References

- 1 A-level Chemistry by EN Ramsden
- 2 Chemistry Longman A–level Guides by JGR Briggs
- 3 Understanding Advanced Organic and Analytical Chemistry by Tan J. and Chan K. S.
- 4 Chemistry The Molecular Nature of Matter and Change by Silberberg

Video Resources

Electrophilic addition mechanism of alkenes Test for alkenes by bromine water





Lecture	1	2
Pages	1–9	10-16
Complete by	25 Aug	3 Sep
Tutorial Qns	1–4	5–7

1 Introduction

- Alkenes belong to the homologous series of hydrocarbons containing a C=C bond.
- General formula: C_nH_{2n}
- The names of all alkenes end with '-ene'. The simplest alkene is ethene, CH₂=CH₂.
- Isomerism occurs in alkenes containing more than three carbon atoms and occurs in three ways.
 - (i) **Constitutional / Chain isomers** due to different arrangement of carbon atoms.
 - (ii) **Constitutional / Position isomers** due to different position of C=C bond.
 - (iii) **Cis-trans isomers** due to restricted rotation / lack of free rotation about C=C bond.
 - E.g. C_4H_8 has four isomers (including both constitutional and *cis-trans* isomers).

CH₂=C(CH₃)₂ 2–methylpropene

CH₃ H

ີດ=ດ

trans-but-2-ene

СΗз

CH₃CH₂CH=CH₂ but–1–ene CH₃ CH₃ C=C H H cis–but–2–ene



Step 1:

Identify the **parent chain** (longest continuous carbon chain containing the C=C bond), name the compound after it by replacing '-ane' ending from alkane containing the same number of carbon atoms by '-ene'.

E.g. CH ₂ =CH ₂	CH ₃ CH=CH ₂
ethene	propene

Step 2:

Identify the **position of the C=C bond**. Number the carbon atoms consecutively from the end of the parent chain which gives the **lower number for the position of the C=C bond**.

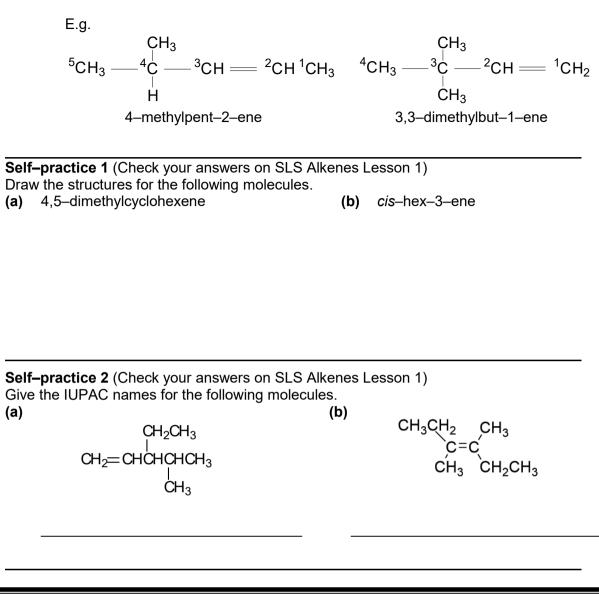
Indicate the position of the C=C bond by placing the number before the syllable '-ene'.

	5	4	3	2	1			1	2	3	4	5	6
E.g.	СН	l₃CH	₂ CH	=C⊦	ICH₃			CH	₃CH	=CF	ICH	₂CH	I_2CH_3
		pen	nt-2-	ene	;				h	ex-	-2–е	ne	

Name the *cis* or *trans* isomer as it is displayed. (See *cis*-but-2-ene and *trans*-but-2-ene as shown above.)

Step 3:

Identify the **alkyl substituent(s)** $(-C_nH_{2n+1})$ attached to the parent chain and **indicate the position(s) of the substituent(s)** based on the numbering system obtained in step 2. Arrange the substituents in **alphabetical order**, ignoring the prefixes such as di– or tri–.



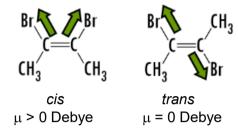
You can now attempt Tutorial Question(s): Q1 – Q2

2 Physical Properties of Alkenes

- The structure and bonding of alkenes are similar to that of alkanes. Hence, they share **similar physical properties with alkanes**.
 - I. Solubility and Density
 - Alkenes are **non-polar**. They are **insoluble in polar solvents** such as **water** but **soluble** in **non-polar solvents** such as CC*l*₄.
 - Alkenes float on water and thus are less dense than water.
 - II. Boiling and Melting Points
 - Boiling point increases with number of carbon atoms as more energy is required to overcome the increasing strength of instantaneous dipole-induced dipole interactions due to increasing number of electrons.
 - Ethene, propene and butene are gases at room temperature, but higher members of alkenes are liquids and then solids.
 - Branched chain isomers have lower boiling points than their straight chain isomers. Branched chain isomers are more spherical with less surface

area of contact between molecules for electron interactions, resulting in a decrease in strength of instantaneous dipole–induced dipole interactions.

• For cis-trans isomers, due to **the larger net dipole moment in the** *cis* **isomer**, it is a polar molecule and is held by **stronger permanent dipole-permanent dipole interactions** and has a **higher boiling point** than the non-polar *trans* isomer.



• However, the *trans* isomer has a higher melting point than the *cis* isomer due to the closer packing of the *trans* isomer molecules.

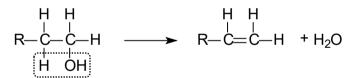
Making Thinking Visible

Question: Why doesn't the closer packing of the trans isomer molecules lead to the trans isomer having a higher boiling point than the cis isomer?

Answer: In the liquid state, the molecules are not rigidly held in fixed positions and they are not very close together as in the solid state. Thus, the packing of molecules is not influential to account for differences in boiling points.

3 Preparation of Alkenes

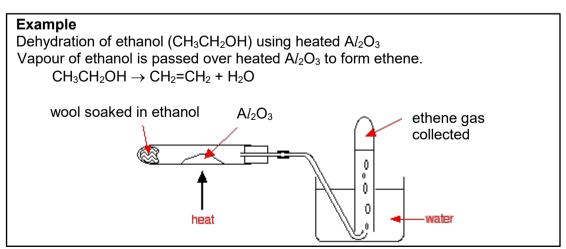
3.1 Dehydration of Alcohols



- Type of reaction: Elimination
- Reagents & conditions: Heat with excess concentrated H₂SO₄

OR

• Reagents & conditions: Heat with Al₂O₃



3.2 Dehydrohalogenation of Halogenoalkanes

$$\begin{array}{ccccc} H & H & H & H \\ I & I \\ R - C - C - H & + & KOH & \longrightarrow & R - C = C - H & + & KX & + & H_2O \\ \hline X & H & (in alcohol) \end{array}$$

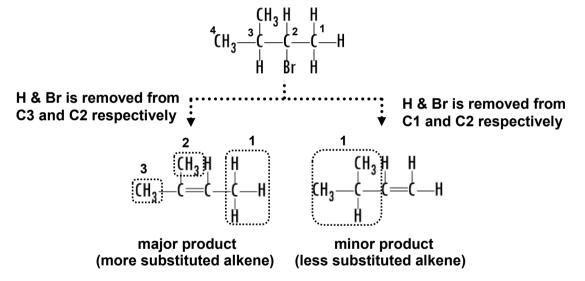
- Type of reaction: Elimination
- **Reagents & conditions:** Heat with KOH in ethanol (or NaOH in ethanol)

Making Thinking Visible

Question: How are KX and H₂O formed in the above reaction?

Answer: An acid–base reaction has happened as shown below: HX (removed from halogenoalkane) + KOH \rightarrow KX + H₂O

- The major product formed is the more stable product which is the more substituted alkene.
 - E.g. There are **two ways to remove one HBr molecule** from the following halogenoalkane.



• How to identify the more substituted alkene?

The more substituted alkene is the one with **more alkyl groups** $(-C_nH_{2n+1})$ **bonded to the C atoms in the C=C bond (inside the dotted boxes)** as shown in the example above. The enthalpy change of hydrogenation of the more substituted alkene to form the corresponding alkane has been found to be less exothermic than its isomeric alkene which is less substituted. This shows that more substituted alkenes are more stable.

For instance, the enthalpy change of hydrogenation of but-2-ene (disubstituted alkene) is less exothermic compared to that of but-1-ene (monosubstituted alkene)

CH₃CH₂CH=CH₂ + H₂ \rightarrow CH₃CH₂CH₂CH₃ Δ H = -125.7 kJ mol⁻¹ (monosubstitued)

CH₃CH=CHCH₃ + H₂ \rightarrow CH₃CH₂CH₂CH₃ Δ H = -118.6 kJ mol⁻¹ (disubstituted)

4 Reactions of Alkenes

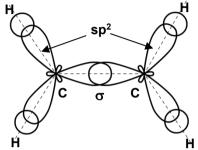
4.1 Electrophilic Addition

Candidates should be able to:

(a) explain the general reactivity of alkenes towards electrophilic reagents/electrophiles

The C=C bond in alkenes consists of a strong sigma bond (σ) and a weak pi (π) bond.

E.g. In CH₂=CH₂,



sp² orbital from each C atom overlaps to form a σ bond in C=C bond

 $2p_z$ orbital from each C atom overlaps laterally to form a π bond in C=C bond

 π molecular orbital

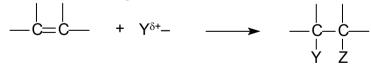
Guiding questions:

- Which classes of reagents do alkenes react with? What types of reactions do alkenes undergo?
- How do alkenes react with electrophiles?
- Since the π electrons are much more exposed than those in the σ bond, this makes the π bond a good source of electrons and the C=C bond is also a region of high electron density. Hence alkenes are more vulnerable to be attacked by electrophiles.

Note: Electrophiles are positively charged ions, e.g. H^+ and NO_2^+ , or polar molecules which carry a partial positive charge, e.g. $H^{\delta+}Cl^{\delta-}$.

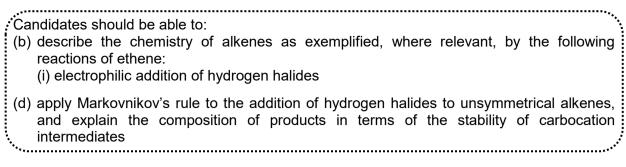
 This availability of π electrons in the C=C bond makes alkenes generally more reactive than alkanes.

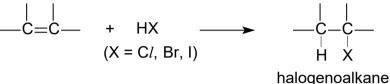
Hence, the typical reaction of alkenes is **electrophilic addition** where **one weak** π **bond is broken** and **two strong** σ **bonds are formed**.



where $Y^{\delta^+}-Z^{\delta^-}$ is an **electrophile** as it contains a **partial positive charged atom**, Y^{δ^+} which has a tendency to attract electrons.

4.11 Addition of hydrogen halides





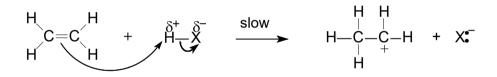
- **Type of reaction:** Electrophilic addition
- Reagent and conditions: HX (g)
- Mechanism:

Case 1

For **symmetrical** alkenes, e.g. ethene $(CH_2=CH_2)$. **Only one product** is formed.

Step 1:

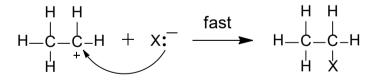
Formation of carbocation by electrophilic attack of $H^{\delta+}$ from the polar $H^{\delta+}-X^{\delta-}$ molecule on the C=C bond.





Step 2:

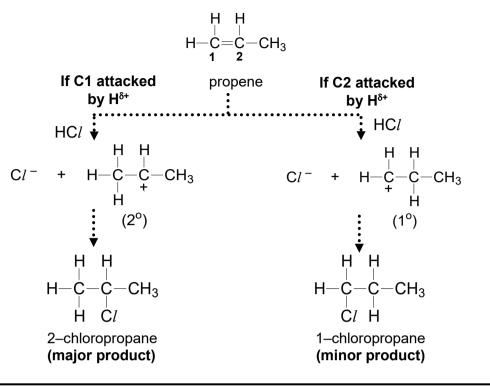
Attack by X⁻ on carbocation.



*MUST show arrow (from lone pair e⁻ to C) to indicate movement of 2 e⁻

Case 2

For **unsymmetrical** alkenes, e.g. propene (CH₃CH=CH₂). **A mixture of two products** are possible, e.g. addition of HC*l* to propene.

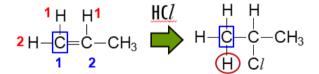


Guiding question:

• How to determine which one is the major product obtained when an unsymmetrical alkene reacts with hydrogen halide?

Markovnikov's Rule in Electrophilic Addition

For unsymmetrical alkenes, e.g. reaction between propene & HCl



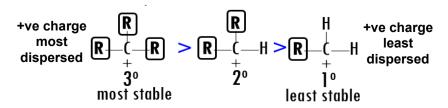
For step 1 of the reaction mechanism, there is electrophilic attack of $H^{\delta+}$ (from $H^{\delta+}Cl^{\delta-}$) to the C atom of the C=C bond having greater number of H atoms directly bonded to it (C1 in this case). Hence, in the above example, 2–chloropropane is the major product.

• Explanation for Markovnikov's Rule

This is to produce a more stable carbocation as the intermediate in the first step of reaction mechanism.

The major product of the electrophilic addition reaction will be the one formed from the more stable carbocation intermediate.

Stability of carbocation: 3° > 2° > 1°



Tertiary (3°) carbocation is the **most stable** as it has **three electron donating alkyl (R) groups**, which exert **electron donating inductive effect** to help **disperse the positive charge on carbocation** more than that of the secondary (2°) and primary (1°) carbocations.

Self-practice 3 (Check your answers on SLS Alkenes Lesson 1)

Suggest reagents and conditions for each of the reactions I and II. Draw the structural formula of the intermediate \mathbf{Q} . [Hint: \mathbf{Q} is an alkene.]

 $\begin{array}{ccc} \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH} \ \rightarrow \ \textbf{Q} \ \rightarrow \ \mathsf{CH}_3\mathsf{CHBrCH}_3 \\ I & II \end{array}$

Solution

[A change in the position of the functional group in the product means that the reactant must undergo elimination of H_2O molecule in step I.]

	Reagents and conditions
Reaction I	
Reaction II	

Q:

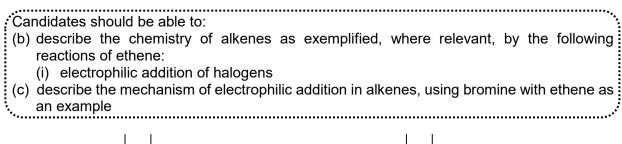
Self-practice 4 (Check your answer on SLS Alkenes Lesson 1)

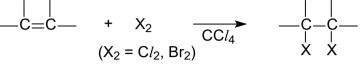
Hydrogen bromide reacts with ethene to form bromoethane. What is the best description of the organic intermediate in this reaction?

- **A** It contains carbon, hydrogen and bromine.
- **B** It has a negative charge.
- **C** It is an electrophile.
- **D** It is a free radical.

You can now attempt Tutorial Question(s): Q3 – Q4

4.12 Addition of halogens in CCl₄





- Type of reaction: Electrophilic addition
- **Reagents and conditions:** X₂ in CCl₄ as solvent

Observation for Br₂: Decolourisation of orange-red bromine in CCl₄

• Mechanism:



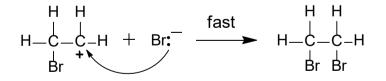
E.g. ethene ($CH_2=CH_2$) reacts with Br_2 in CCl_4

Step 1: Formation of carbocation.

The electron cloud of pi (π) bond in ethene polarises an approaching Br₂ molecule. The partially positive end of the polarised bromine molecule attacks ethene.



Step 2: Attack by Br⁻ on carbocation.



Note:

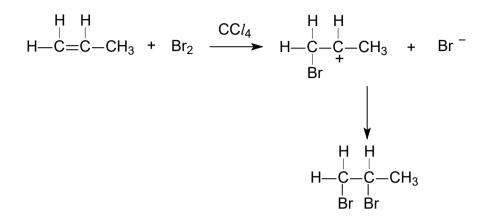
If the reaction is done in the presence of other anions, such as Cl^- or NO_3^- , these anions also attack the carbocation in step 2. Products of the reaction will also include CH_2BrCH_2Cl and $CH_2BrCH_2NO_3$ respectively.

Case 2

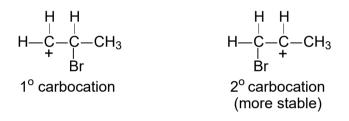
For unsymmetrical alkenes:

E.g. propene (CH₃CH=CH₂) reacts with Br₂ in CCl₄

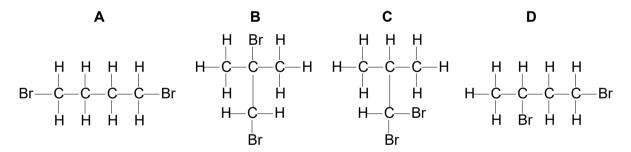
The intermediate formed is the more stable carbocation.



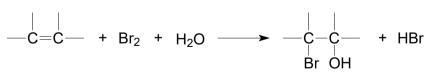
Based on the **Markovnikov's Rule** in **4.11** (pg 8 & 9), the **2**° **carbocation is formed** as the intermediate as it is **more stable** than the 1° carbocation.



Self-practice 5 (Check your answer on SLS Alkenes Lesson 2) Which compound could be formed by the action of bromine on an alkene of formula C_4H_8 ?



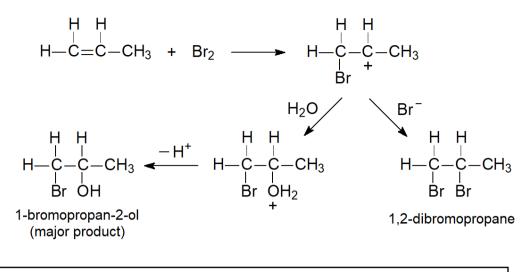
4.13 Addition of halogens in water



- **Type of reaction:** Electrophilic addition
- Reagents and conditions: Br₂ in water or Br₂(aq)

Observation: Decolourisation of orange aqueous bromine

• Mechanism:



Making Thinking Visible

- **Question:** For the reaction of propene with Br₂(aq), why is 1–bromopropan–2–ol the major product and 1,2–dibromopropane the minor product?
- **Answer:** H₂O molecules are present in a larger quantity as water is the solvent. Thus, the probability of the carbocation reacting with H₂O is much higher than the probability of the carbocation reacting with Br⁻.

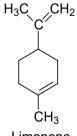
Self-practice 6 (Check your answer on SLS Alkenes Lesson 2)

Which compounds would be formed in the reaction of ethene with aqueous bromine in the presence of sodium chloride?

1 CH_2C/CH_2Cl **2** CH_2BrCH_2Cl **3** CH_2BrCH_2Br

Self-practice 7 (Check your answer on SLS Alkenes Lesson 2)

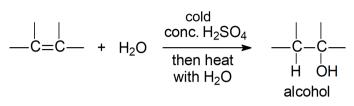
Limonene is an oil formed in the peel of citrus fruits. Draw the structural formula of the product formed when aqueous bromine reacts with limonene at room temperature.



4.14 Addition of water

Candidates should be able to:

- (b) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
 - (i) electrophilic addition of water/steam



• **Type of reaction:** Electrophilic addition

• Reagent and condition:

cold concentrated H₂SO₄, followed by heat with water

OR steam, high temperature, high pressure, H₃PO₄ catalyst

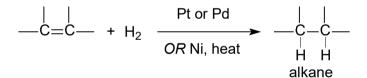
Note:

This is the reverse of the method used to prepare alkene from alcohol and concentrated H_2SO_4 .

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4.2 Reduction

Candidates should be able to: (b) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene: (iii) reduction via catalytic hydrogenation (catalytic addition of hydrogen)



- Type of reaction: Reduction
- Reagent & conditions: H₂(g) with Pt or Pd catalyst

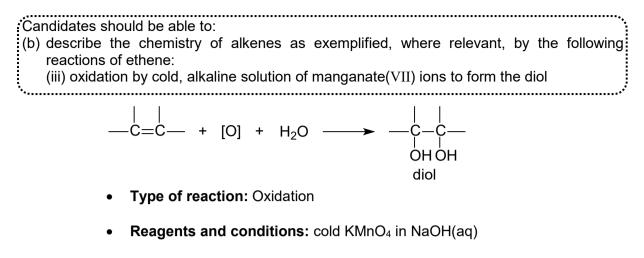
OR

Reagent & conditions: Heat with H₂(g) and Ni catalyst

4.3 Oxidation

- 4.31 Combustion
 - In excess oxygen, alkenes burn to give carbon dioxide and water.
 E.g. C₂H₄(g) + 3O₂(g) → 2CO₂(g) + 2H₂O(I)
 - In limited oxygen, alkenes may burn to give carbon monoxide and water.
 E.g. C₂H₄(g) + 2O₂(g) → 2CO(g) + 2H₂O(l)
 - Combustion occurs with a more smoky flame than alkanes due to the greater C:H ratio in alkenes. [E.g. 1/3 in C₂H₆ vs 1/2 in C₂H₄]

4.32 Formation of diol (mild oxidation)



Observation: Purple KMnO₄ decolourised with formation of brown precipitate, MnO₂

• When there is no heating, mild oxidation of the C=C bond will take place where only the π bond is broken and a diol is formed.

4.33 Formation of carboxylic acids, ketones and/or CO₂ (strong oxidation)

Candidates should be able to: (b) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions
of ethene: (iv) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon–to–carbon double bond in order to determine the position of alkene linkages in
larger molecules

- **Type of reaction:** Oxidative cleavage
- Reagents and conditions: KMnO₄ in H₂SO₄(aq), heat

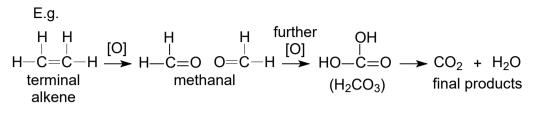
Observation: Purple KMnO₄ decolourised

• When heated, there will be strong oxidation of the C=C bond and oxidative cleavage of C=C bond occurs. The π bond in the C=C bond is first cleaved, followed by the cleavage of the C-C σ bond.

• There are 3 possibilities for cleavage of C=C bond.

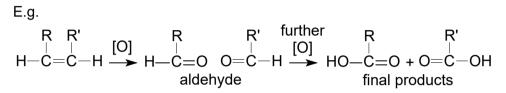
Case 1

=CH₂ group which occurs in a terminal alkene is oxidised to CO₂



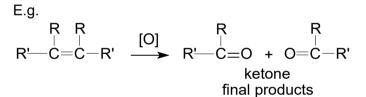
Case 2

=CHR group in an alkene is oxidised to a carboxylic acid (RCO₂H)

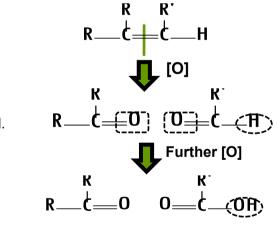


Case 3

=CRR' group in an alkene is oxidised to a ketone (RCOR')



 In summary, to identify the cleavage products of the oxidation of various alkenes with acidic KMnO₄:

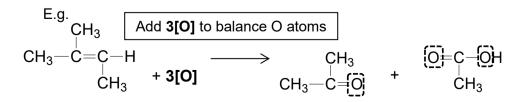


Step 2: Attach O atom to C= bond.

Step 3: Replace – H with – OH.

Step 1: Cleavage of C=C bond.

• Oxidation equation for alkenes is expressed by using [O] notation.



Self-practice 8 (Check your answers on SLS Alkenes Lesson 2)

Predict the carbon–containing products when the following alkene reacts with an aqueous solution of potassium manganate(VII) under acidic and alkaline conditions.

 $CH_2=C-CH=CHCH_3$

cold, alkaline KMnO ₄	hot, acidified KMnO4	hot, alkaline KMnO₄			
Note: A diol is formed at <u>cold/room</u> temperature.	Note: C=C cleaves as temperature is <u>high</u> .	Note: C=C cleaves as temperature is <u>high</u> . <u>Salts</u> , not acids, are obtained in alkaline solution.			

Self-practice 9 (Check your answer on SLS Alkenes Lesson 2)

 CH_3 CH_3 H_3C — $\dot{C}=0$ and $O=\dot{C}-OH$ are the only two carbon–containing products from the oxidation of an alkene with hot acidified KMnO₄. Determine the identity of the alkene.

You can now attempt Tutorial Question(s): Q5 – Q7

5 Tests for Alkenes

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- A good test for an organic compound should give an **observable visual result** where there is
 - (a) a colour change, or
 - (b) a precipitate formed and the colour of the precipitate, or
 - (c) a gas given off and identify the gas.
- The following test could be used to indicate the **presence of C=C bond** in alkenes.

Decolourisation of a solution of **orange–red** Br₂ in CCl₄ or **orange** Br₂ in H₂O.

6 Summary

• Preparation of Alkenes

Reaction	Reagents & conditions	Example of balanced equations
From alcohols	Excess conc. H ₂ SO ₄ , heat OR Al ₂ O ₃ , heat	$CH_{3}CH_{2}CH_{2}OH \\ \rightarrow CH_{3}CH=CH_{2} + H_{2}O$
From halogenoalkanes	NaOH or KOH in ethanol, heat	$CH_3CH_2CH_2Br + KOH(ethanol)$ $\rightarrow CH_3CH=CH_2 + KBr + H_2O$

• Reactions of Alkenes

Type of reaction	Reagents & conditions	Examples of balanced equations
		$CH_3CH=CH_2 + HBr \rightarrow CH_3CHBrCH_3$
	HBr(g)	(Follow Markovnikov's rule: H of HBr is attached to carbon atom of C=C bond which has more hydrogen atoms directly bonded to it.)
	Br ₂ in CCl ₄	$CH_{3}CH=CH_{2} + Br_{2} \rightarrow CH_{3}CHBrCH_{2}Br$
		Decolourisation of orange-red bromine in CCl ₄ .
		$CH_3CH=CH_2 + Br_2 + H_2O$
		\rightarrow CH ₃ CH(OH)CH ₂ Br + HBr
Electrophilic addition	Br₂(aq)	Decolourisation of orange aqueous bromine.
		(Follow Markovnikov's rule: Br is attached to carbon atom of C=C bond which has more hydrogen atoms directly bonded to it.)
	cold concentrated H ₂ SO ₄ , followed by heat with water OR steam, high temperature, high pressure, H ₃ PO ₄ catalyst	CH ₃ CH=CH ₂ + H ₂ O → CH ₃ CH(OH)CH ₃ (Follow Markovnikov's rule: H of H ₂ O is attached to carbon atom of C=C bond which has more hydrogen atoms directly bonded to it.)
Reduction	H ₂ , Pt or Pd catalyst OR H ₂ , Ni catalyst, heat	$CH_3CH=CH_2 + H_2 \rightarrow CH_3CH_2CH_3$
	O ₂ (combustion)	$CH_3CH=CH_2 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O$
Oxidation	cold KMnO₄ in NaOH(aq)	$CH_{3}CH=CH_{2} + [O] + H_{2}O$ $\rightarrow CH_{3}CH(OH)CH_{2}(OH) \text{ (diol)}$
		$CH_3CH=CH_2 + 5[O] \rightarrow CH_3CO_2H + CO_2 + H_2O$
Oxidative cleavage	KMnO₄ in H₂SO₄(aq), heat	In general, $RCH=CR_2 + 3[O] \rightarrow RCO_2H + RCOR$ (carboxylic acid) (ketone) $RCH=CH + 5[O] \rightarrow RCO_2H + CO_2H + CO_2$
		RCH=CH ₂ + 5[O] → RCO ₂ H + CO ₂ + H ₂ O terminal alkene

Note: If no heat is written for a reaction, it means that the reaction can take place at room temperature.