Chem Factsheet

www.curriculum-press.co.uk Number 92

Electrophilic Addition

To succeed in this topic you need to:
- **understand the nature of the C=C covalent bond in terms of σ- and π-orbitals (covered in Factsheet 87);**
- **know the reactions of alkenes (covered in Factsheet 16).**

After working through this Factsheet you will:
- **understand the principles of electrophilic addition to alkenes;**
- **be able to write mechanistic equations for the reactions of alkenes with halogens, hydrogen halides and sulphuric acid;**
- **know that carbocations (carbonium ions) are classified as primary, secondary or tertiary;**
- **understand that the stability of carbocations increases from primary to secondary to tertiary;**
- **know that, when unsymmetrical alkenes react with hydrogen-containing reagents, there are two possible products;**
- **be able to explain the formation of one product rather than another in terms of the stability of carbocations.**

All organic reactions are classified on a mechanistic basis into the following caregories:
- substitution;
- addition;
- elimination;
- rearrangenent.

> ***Exam Hint*** *- Wherever possible, when you are asked to state the type of an organic reaction, you should give the mechanistic classification. Try to avoid synthetic descriptions, such as hydrolysis, chlorination or nitration.*

For compounds to take part in addition reactions, their molecules must contain multiple bonds, notably C=C (in alkenes) and C=O (in aldehydes and ketones).

> ***Remember*** *- Addition means 'combination'.*
> *In an addition reaction, the reagent (i.e. the attacking molecule) combines with the substrate (molecule that is being attacked) to give one product only, known as an addition product or 'adduct'.*

Addition reactions are subdivided according to the nature of the attacking species.
- Electrophilic addition - shown by alkenes.
- Free radical addition - shown by alkenes under conditions that favour the formation of free radicals, especially the presence of ultraviolet light. (Not required at A-level)
- Nucleophilic addition - shown by aldehydes and ketones.

Why are alkenes subject to electrophilic addition?
You need to understand the nature of both electrophiles and alkenes.

> *An electrophile is defined as an attacking species which seeks out, for its attack, an electron-rich centre in the substrate.*
> *For a species to act as an electrophile, it must satisfy the following three basic requirements.*
> 1. *It must contain an atom with a positive electrical charge. For maximum attraction to the electron-rich centre of the substrate, an electrophile should carry a full positive charge, i.e. it should be ionic, but in practice most electrophiles are polar molecules in which there is an atom with a partial positive charge.*
> 2. *Its positively charged atom must have a vacant orbital at a relatively low energy level to accommodate an incoming pair of electrons.*
> 3. *It must be able to form a strong bond with a carbon atom, otherwise there cannot be a stable reaction product.*

The nature of the carbon-carbon double bond in alkenes is fully described in Factsheet 87.

> ***Remember*** *- The two covalent bonds of a C=C bond are not identical with each other. One, called a σ-bond, is similar to a C-C single bond. It is strong and not broken during addition reactions. The other, called a π-bond, is relatively weak. This is the one which is broken during electrophilic addition.*

Alkenes undergo electrophilic addition with halogens, hydrogen halides and sulphuric acid.

> *- All these reactions have the following features in common.*
> - *The reagent is polarised* $\overset{\delta+}{X}—\overset{\delta-}{Y}$
> - *The atom with the partial positive charge (*δ^+*) is attracted to, and accepts, the two π-electrons of the C=C bond.*
> - *The bond X-Y undergoes* heterolytic fission, *i.e. it becomes broken in such a way that both the electrons of the bond go to* $Y^{\delta-}$.
> - X^+ *does not become free (too much energy is required for this) but bonds permanently to one of the atoms of the C=C bond to give a* carbocation *or* carbonium ion, *i.e. an ion in which positive charge is located on a C atom.*
> - Y^- *is a* nucleophile, *i.e. a negatively charged species, capable of donating a lone pair of electrons, which will seek out a positive centre for its attack.*
> - *In the final stage of the mechanism,* Y^- *coordinates to the carbocation to give the adduct.*

Reactions with halogens

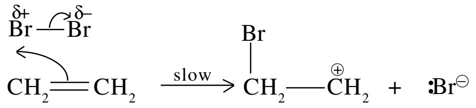
Bromine reacts with alkenes at room temperature to give 1,2-dibromides. Reactions are usually carried out in an organic solvent, such as hexane or trichloromethane.

E.g. $CH_2{=}CH_2 + Br_2 \rightarrow CH_2Br\text{-}CH_2Br$
1,2-dibromoethane

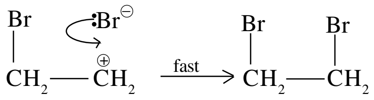
Chlorine also reacts readily, but with iodine there is no reaction.

The mechanism follows the principles shown above. It is perhaps surprising that bromine, a non-polar substance, should react in this way: indeed, it has been reported that a mixture of an alkene and pure, dry bromine in PTFE apparatus will not react together. However, traces of water or the surface of glass apparatus - conditions that commonly exist - are sufficient to induce temporary polarisation in the Br_2 molecule. The mechanism is summarised by the two equations shown below. Notice particularly the use of 'curly arrows' to show the movement of pairs of electrons.

> ***Exam Hint*** *- Be very careful how you draw curly arrows!*
> - *A 'curly arrow' is used to show the movement of a pair of electrons.*
> - *The arrow must be curved and have a complete arrowhead.*
>   *(A half-arrow is used to show the movement of a single electron.)*
> - *It must start from the original location of the electron pair and point to where it finishes up.*
> - *It must NEVER start from or point to an electrical charge.*



(Examiners may allow curly arrow pointing to $Br^{\delta+}$.)



(Examiners may allow curly arrow pointing to $C^{\oplus}$.)

> ***Exam Hint -*** *To make sure of maximum marks, when asked to give this mechanism, you must:*
> - *describe the mechanism as electrophilic addition (not just 'addition');*
> - *write mechanistic equations;*
> - *make sure the curly arrows and the carbocation are correctly drawn;*
> - *mention heterolytic fission of Br_2.*

Evidence for this mechanism is provided by carrying out the reaction in the presence of chloride ions. The product is a mixture of $CH_2Br\text{-}CH_2Br$ and $CH_2Br\text{-}CH_2Cl$, suggesting that, in the final stage, Br^- and Cl^- are competing for the carbocation, $CH_3CH_2^{\oplus}$.

Reaction with hydrogen halides

Alkenes react with concentrated hydrobromic acid at 100 °C to give bromoalkanes, e.g.

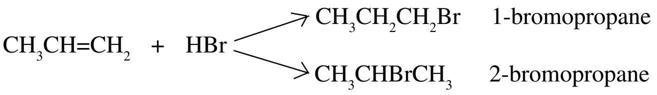
$$CH_2{=}CH_2(g) + HBr(aq) \rightarrow CH_3CH_2Br(l)$$

Hydriodic acid behaves in a similar manner but there is no reaction with hydrochloric acid. (Hydrogen chloride gas will react if heated to about 200 °C.)

The HBr molecule is permanently polarised, $H^{\delta+}\text{—}Br^{\delta-}$, and reacts with alkenes by an identical mechanism to Br_2.

Hydrogen bromide with unsymmetrical alkenes

When propene reacts with HBr, there are two possible adducts:



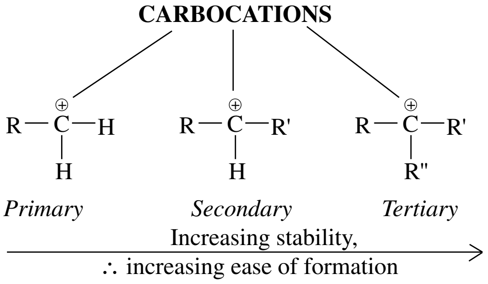
$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CH_2CH_2Br \quad \text{1-bromopropane}$$
$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3 \quad \text{2-bromopropane}$$

In fact, the product is almost entirely 2-bromopropane. Markownikoff's rule helps you to predict this.

> *Markownikoff's rule states that, whenever a hydrogen-containing reagent reacts with an unsymmetrical alkene, the incoming hydrogen atom goes to the carbon atom of the double bond with the most hydrogen atoms already joined to it. (As sociologists say, 'The rich get richer.')*

To understand this, you must know that carbocations vary in their stability. They are classified as primary, secondary or tertiary, depending on whether the positive charge is located on a primary, secondary or tertiary carbon atom, and increase in stability from primary to secondary to tertiary.

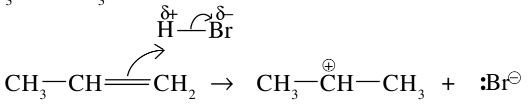
> ***Remember*** *- A primary carbon atom is attached to one alkyl radical (R), a secondary carbon atom is attached to two alkyl radicals, and a tertiary carbon atom is joined to three.*



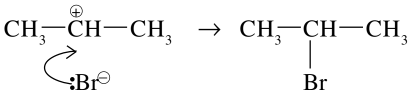
The increase in stability is due to the fact that positive charge can be shared with alkyl groups (R) but not with H atoms. The sharing or *delocalisation* of electrical charge, anywhere in physical science, always leads to greater stability. Tertiary carbocations, with three alkyl groups, allow maximum delocalisation and are particularly stable. Because they are at a low energy level, relatively little energy is required for their formation and they are therefore formed preferentially. If a tertiary carbocation cannot be formed you get a secondary one; failing that, a primary one.

> *Whenever there are competing mechanistic routes for electrophilic addition, reaction occurs preferentially through the more stable carbocation.*

In the case of propene and HBr, the main product is 2-bromopropane because it is formed via the relatively stable secondary carbocation, $CH_3\text{-}\overset{\oplus}{C}H\text{-}CH_3$.



(Examiners may allow curly arrow to $H^{\delta+}$.)



(Examiners may allow curly arrow to $C^{\oplus}$.)

The alternative product, 1-bromopropane, could be formed only via the relatively unstable primary carbocation, $CH_3\text{-}CH_2\text{-}\overset{\oplus}{C}H_2$.

Exam Hint *- An explanation for the formation of one product of electrophilic addition rather than another is commonly asked for in examinations. There are three traps for the unwary.*

- *NEVER say that one product is formed rather than another "because this is in accordance with Markownikoff's rule." This is rather like saying that "A is formed rather than B because Markownikoff says so." Markownikoff does not control organic chemistry! His law is merely a statement of experimental findings and has no regard for causes.*
- *Always argue on the basis of the stability of carbocations; NOT on the stability of final products.*
- *Tailor your answer to the question. Just saying that "A is formed rather than B because secondary carbocations are more stable than primary carbocations" will not get you full marks. E.g. in answer to the propene with HBr question, you should say that the main product is 2-bromopropane because it is formed via the relatively stable secondary carbocation, $CH_3\overset{\oplus}{C}HCH_3$.*

Reaction with sulphuric acid

Electrophilic addition also occurs when alkenes are absorbed by cold concentrated sulphuric acid.

Exam Hint *- Always distinguish between concentrated and dilute sulphuric acid. NEVER just write 'sulphuric acid'.*

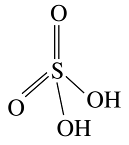
The products are alkyl hydrogen sulphates, e.g.

$$CH_2{=}CH_2 \;+\; H_2SO_4 \rightarrow CH_3CH_2OSO_2OH$$

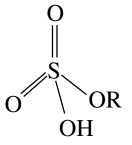
Ethyl hydrogen sulphate

Markownikoff's rule applies to the addition of sulphuric acid to unsymmetrical alkenes. Propene, for example, reacts to give 1-methylethyl hydrogen sulphate (isopropyl hydrogen sulphate).

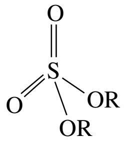
Alkyl hydrogen sulphates are half-esters of sulphuric acid:



Sulphuric acid



Alkyl hydrogen sulphate (Half-ester)

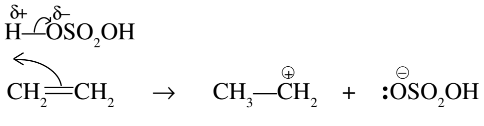


Dialkyl sulphate (Full ester)

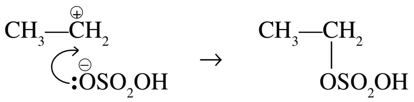
Concentrated sulphuric acid is almost pure sulphuric acid and, for all practical purposes, consists of polarised molecules;

$\overset{\delta+}{H}\text{-}\overset{\delta-}{O}\text{-}SO_2\text{-}OH$ rather than ions H^+ and HSO_4^-.

Reaction mechanisms are therefore closely similar to those shown above.



(Examiners may allow curly arrow to $H^{\delta+}$.)



(Examiners may allow curly arrow to $C^{\oplus}$.)

Like all other esters, an alkyl hydrogen sulphate can be hydrolysed to give an acid and an alcohol. Hot water is enough to hydrolyse ethyl hydrogen sulphate:

$$C_2H_5OSO_2OH \;+\; H_2O \;\rightarrow\; C_2H_5OH \;+\; H_2SO_4$$

Ethanol and sulphuric acid are readily separated by distillation. This provides the answer to a favourite exam question, 'How would you convert ethene into ethanol?'

Exam Hint *- Whenever you are asked how you would carry out a conversion, never quote an industrial process. The examiner assumes that YOU would be working in a laboratory with the usual lab reagents and equipment. Students often make the mistake of saying that they would convert ethene into ethanol by adding steam, compressing the mixture to 70 atm and then passing it over a phosphoric acid catalyst maintained at 300 °C. This so-called direct hydration of ethene is, of course, the industrial method of producing synthetic ethanol.*

Conversely, never quote laboratory chemistry when asked about industrial processes.

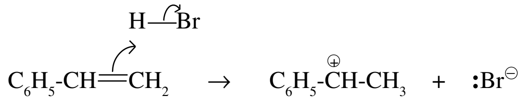
Practice questions

1. Although the HCN molecule is polarised, $\overset{\delta+}{H}\text{—}\overset{\delta-}{CN}$, hydrogen cyanide does not undergo electrophilic addition to alkenes. Explain this.
2. Write mechanistic equations for the following reactions.
   (a) Phenylethene (styrene) with hydrogen bromide.
   (b) Propene with concentrated sulphuric acid.
3. Carbocations have a positive charge residing on a carbon atom. Suggest why it is that a carbon atom can share its charge with adjoining alkyl groups, such as CH_3.
4. Suggest why, when ethene reacts with bromine water, 2-bromoethanol is formed as well as 1,2-dibromoethane.

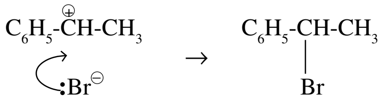
Answers

1. The H-C bond is particularly strong. (Its average bond enthalpy is 412 kJ mol^{-1}.) A prohibitively large amount of energy would be needed for heterolytic fission of the bond.

2. (a)

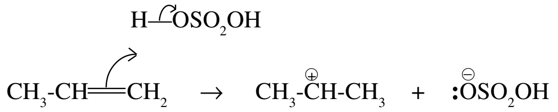


(Examiners may accept curly arrow to H.)

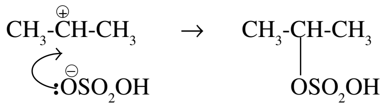


(Examiners may accept curly arrow to $C^{\oplus}$.)

(b)



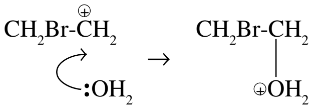
(Examiners may accept curly arrow to H.)



(Examiners may accept curly arrow to $C^{\oplus}$.)

3. Alkyl groups have a positive inductive (+I) effect, i.e. electron releasing effect. This reduces the positive charge on $\overset{\oplus}{C}$ and, at the same time, causes partial positive charge to develop on the methyl group.

4. The H_2O molecule is a nucleophile which, in the final stage of the mechanism, competes with $Br^{\ominus}$ for the carbocation, $CH_2Br\text{-}CH_2$.



Loss of a proton from this protonated alcohol gives $CH_2Br\text{-}CH_2OH$.

Acknowledgements: *This Factsheet was researched and written by John Brockington.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***