Chem Factsheet

www.curriculum-press.co.uk Number 226

Carbocations

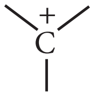
"Cation" is the general term for a positively charged ion. Metals generally lose electrons when they react and so form the most common cations such as Na^+, Mg^{2+} and Al^{3+}. However, an ion such as ammonium (NH_4^+) is also a cation but its charge is on a non-metallic nitrogen atom. H^+ and H_3O^+ also fit into this category.

The term arises from the Greek word "kata" meaning "down" – *down* in the sense that it is a particle with fewer electrons (negatively charged) than protons (positively charged) in total, making it positively charged overall.

This derivation is also seen in the term "**cat**hode" – the negatively charged electrode that attracts **cat**ions in an electrolytic cell.

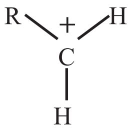
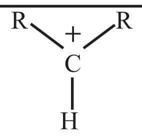
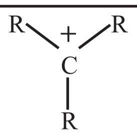
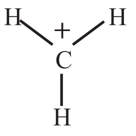
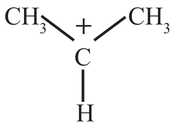
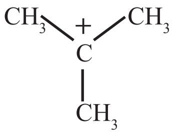
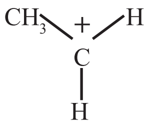
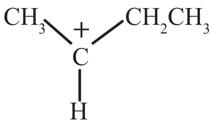
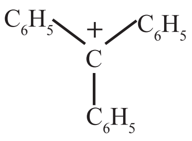
A **carb**ocation is therefore a particle with a positive charge on a **carb**on atom. They are also sometimes called *carbonium* ions. Unlike the common cations mentioned above, carbocations do not generally occur naturally. They arise transiently as reaction intermediates and during mass spectrometry.

A carbon atom has 4 electrons in its outer electron shell and will therefore generally form 4 covalent bonds. However, for a positively charged carbon atom in a carbocation, one of these electrons has been lost resulting in the charged C atom having only 3 covalent bonds.



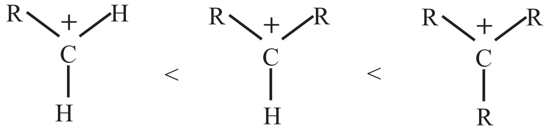
Classification

Carbocations are classified as primary, secondary or tertiary depending on the number of H atoms bonded to the C^+ atom. These are summarised in the following table.

Primary	Secondary	Tertiary
2 or more H atoms bonded to the C^+ atom	Only one H atom bonded to the C^+ atom	No H atoms bonded to the C^+ atom
 ($R = C_nH_{2n+1}$ or C_6H_5)	 ($R = C_nH_{2n+1}$ or C_6H_5)	 ($R = C_nH_{2n+1}$ or C_6H_5)
e.g. Methyl carbocation 	e.g. Secondary propyl 	e.g. Tertiary butyl 
e.g. Ethyl carbocation 	e.g. Secondary butyl 	e.g. Triphenyl methyl 

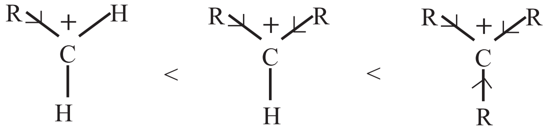
Relative stabilities of carbocations

In general, carbocation stability INCREASES from primary to secondary and from secondary to tertiary.

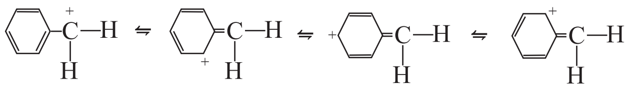


But why is this? The inherent instability of a carbocation is caused by the positive charge concentrated on a C atom – C atoms are associated with covalent bonding, not ionic! If the concentration of positive charge on the C atom can be reduced, the ion will be relatively more stable.

(a) For $R = C_nH_{2n+1}$
Alkyl groups push electrons away from themselves. This is called their "positive inductive effect". As electron density is pushed towards the C^+ atom (see below – shown by > on covalent bond), the net positive charge on the C^+ atom is reduced and hence, the stability of the carbocation increased. For primary carbocations there is a maximum of one alkyl group causing this effect but secondary and tertiary carbocations have two and three alkyl groups respectively resulting in increasing reduction of positive charge on C+ and consequent increasing stability.



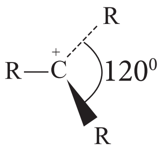
(b) For $R = C_6H_5$
Delocalised aryl groups can extend their delocalisation to include the C^+ atom and so spread the + charge over the entire particle as shown below. This delocalisation also increases the stability of the carbocation. In fact it is far more stabilising than the positive inductive effect discussed in (a).



The carbocation which contains 3 phenyl groups is so stable that it can exist as an ion. Hence, chlorotriphenylmethane conducts electricity when dissolved in liquid sulphur dioxide because it is ionised to the triphenyl carbocation and a chloride ion. $(C_6H_5)_3C\text{-}Cl \rightarrow (C_6H_5)_3C^+ + Cl^-$

Geometry of carbocations

In general the three bonds to the C^+ atom tend to arrange themselves as far apart as possible to minimise repulsions. Hence, carbocations are generally planar around the C^+ atom with the 3 bonds at 120° to each other.



This is particularly important in controlling the optical activity of some reaction products – see later.

Carbocations during mass spectrometry

Briefly, during mass spectrometry, a molecule (M) is converted to a molecular ion-radical ($M^{+\bullet}$) by bombardment with high energy electrons which knocks an electron out of the molecule.

$$M(g) + e- \rightarrow M^{+\bullet}(g) + 2e-$$

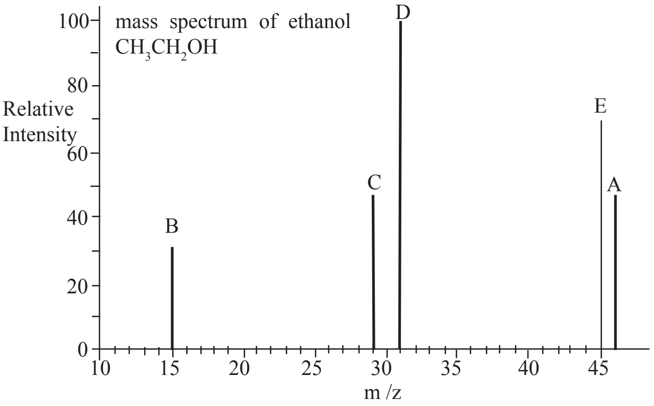
The molecular ion-radical then fragments by the breaking of some or more of its covalent bonds forming various fragment carbocations [$F^+(g)$] and free radicals [$R^\bullet(g)$] depending on which bond breaks.

$$M^{+\bullet}(g) \rightarrow F^+(g) + R^\bullet(g)$$

e.g. Ionisation and fragmentation of ethanol produces results in the molecular ion-radical and various fragment carbocations according to the following equations

Ionisation : $CH_3CH_2OH \rightarrow [CH_3CH_2OH]^{+\bullet} + e-$
Fragmentation via C-H bond : $[CH_3CH_2OH]^{+\bullet} \rightarrow [CH_2CH_2OH]^+ + H^\bullet$
Fragmentation via O-H bond : $[CH_3CH_2OH]^{+\bullet} \rightarrow [CH_3CH_2O]^+ + H^\bullet$
Fragmentation via C-O bond : $[CH_3CH_2OH]^{+\bullet} \rightarrow [CH_3CH_2]^+ + {}^\bullet OH$
Fragmentation via C-C bond : $[CH_3CH_2OH]^{+\bullet} \rightarrow [CH_3]^+ + {}^\bullet CH_2OH$
and $[CH_3CH_2OH]^{+\bullet} \rightarrow [CH_3]^\bullet + [CH_2OH]^+$

The carbocations, but not the free radicals, are detected and measured to give the characteristic mass spectrum.



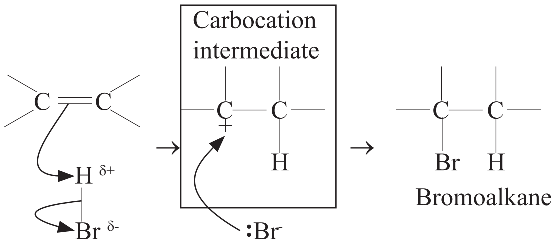
A – $[CH_3CH_2OH]^{+\bullet}$ molecular ion-radical
B – $[CH_3]^+$ carbocation
C – $[CH_3CH_2]^+$ carbocation
D – $[CH_2OH]^+$ carbocation
E – $[CH_2CH_2OH]^+$ carbocation and $[CH_3CH_2O]^+$ cation

The relative stabilities of the different types of carbocation can also be inferred from mass spectra. Consider the isomers 1-chlorobutane, 2-chlorobutane and 2-chloro-2-methylpropane. If each of these is ionised and the fragmentation of the Cl atom as free radical considered, then a primary, a secondary and a tertiary carbocation respectively will be produced as shown in the following table.

The ratios show that there is a preponderance of the tertiary carbocation because it is the most stable type – once formed it is less likely to break down further. Similarly, the secondary carbocation is more likely than the primary carbocation to form, and not be further fragmented.

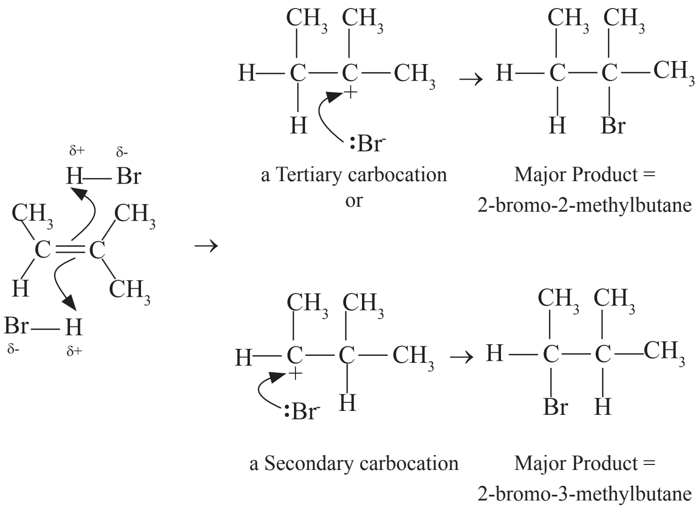
Carbocations during electrophilic addition reactions

As shown in the following general mechanism for the electrophilic addition of HBr to an alkene, the intermediate particle is a carbocation.



The initial bonding of the H^+ electrophile to a C atom could occur at either C atom of the C=C bond, possibly producing two different carbocations. Depending on the identity of the alkene, these intermediate carbocations may be primary, secondary or tertiary. If there is a choice of carbocation type, the reaction will proceed preferentially via the more stable carbocation type leading to a major addition product. The reaction will also happen to a lesser extent via the less stable carbocation type leading to a minor addition product. If the alkene is non-symmetrical, the overall product will always be a mixture of compounds.

This is shown in the following diagram where HBr is added to 2-methyl-but-2-ene.



Bonding of the H^+ electrophile to the C=C bond of 2-methyl-but-2-ene produces two possible carbocations, as shown. One is tertiary and the other is secondary. The major product is formed via the more stable tertiary ion and the minor product via the less stable secondary ion, after bonding of the respective carbocations to the bromide ion.

Isomer	1-chlorobutane	2-chlorobutane	2-chloro-2-methylpropane
Formula	$CH_3CH_2CH_2CH_2Cl$	$CH_3CHClCH_2CH_3$	$(CH_3)_3CCl$
Carbocation	$CH_3CH_2CH_2C^+H_2$	$CH_3C^+HCH_2CH_3$	$(CH_3)_3C^+$
Type	Primary	Secondary	Tertiary
Ratio of carbocation peak to molecular ion peak	40:1	56:1	65:1

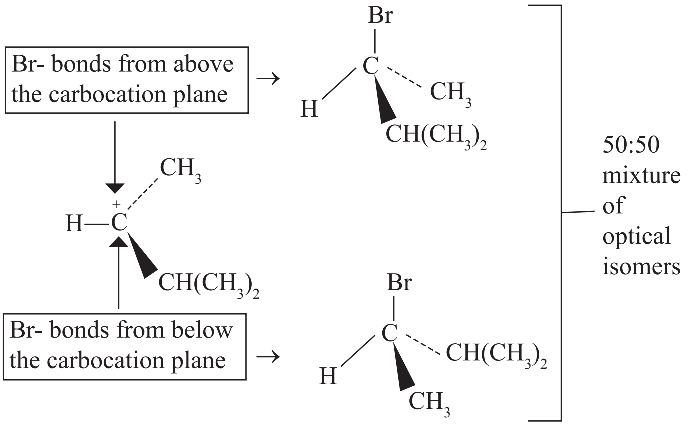
Racemisation during electrophilic addition reactions

> Racemisation is the formation of a racemic mixture during the course of a reaction. i.e. the formation of an optically inactive, equimolar mixture of optical isomers (a.k.a. enantiomers – non-superimposable mirror images of each other).

If the C+ atom in a carbocation is bonded to 3 *different* groups, bonding to the Br^- ion gives 4 different groups bonded to the same C atom. This is the basic requirement for the existence of optical isomers.

Furthermore, as noted earlier, the 3 bonds around the C^+ atom in a carbocation are planar and bonding of the Br^- ion is equally likely to occur above or below this plane resulting in a 50:50 mixture of the optical isomers. Racemisation has occurred!

This can be illustrated using the secondary carbocation intermediate from the previous example. This has the required 3 different groups – H, CH_3 and $CH(CH_3)_2$.

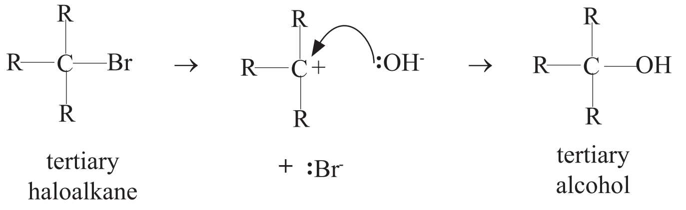


Hence, the *minor* product in the addition of HBr to 2-methyl-but-2-ene will be produced as a racemic mixture.

Carbocations during nucleophilic substitution reactions

When a *tertiary* bromoalkane (CR_3Br – all 3 R groups being alkyl groups) reacts with aqueous sodium hydroxide, the bromine atom is substituted by the hydroxide nucleophile to form an alcohol.
The mechanism involves a two-step process

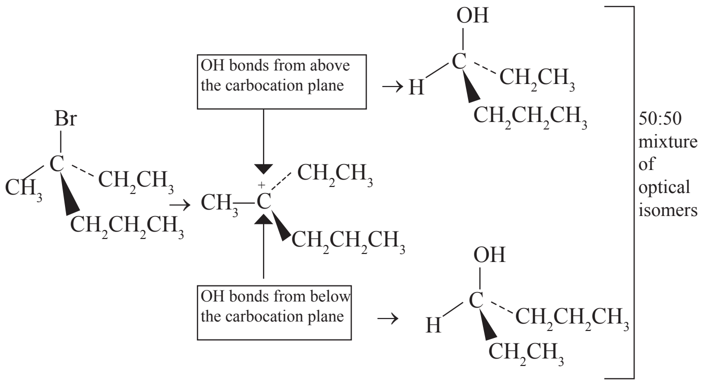
(1) the ionisation of the C-Br bond to form a tertiary carbocation followed by
(2) combination of the carbocation with a hydroxide ion to form the product.



> In some specifications this is called the SN_1 mechanism – ***S****ubstitution* ***N****ucleophilic with overall order of reaction* ***1***. Primary, and to some extent secondary bromoalkanes, do not react like this – they react by a one-step process (SN_2) which does not involve a carbocation intermediate – the C-Br bond breaking and C-O bond formation occur simultaneously. The difference arises because of the higher stability of the tertiary carbocation promotes the 2 step process.

Racemisation during nucleophilic substitution reactions

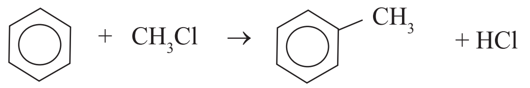
If the haloalkane is optically active (3 *different* R groups + Br bonded to the central carbon) then, when the hydroxide ion combines with the intermediate planar tertiary carbocation, it can bond from above or below the plane with equal probability. This leads to the formation of a racemic mixture of the alcohols as shown in the following example.



Carbocations during Friedel-Crafts alkylation reactions

This is the reaction of benzene (or a related compound) with a haloalkane in the presence of an anhydrous aluminium chloride catalyst to form an alkylbenzene by electrophilic substitution.

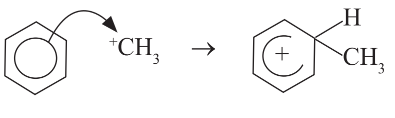
e.g. Benzene + Chloromethane → Methylbenzene + Hydrogen chloride



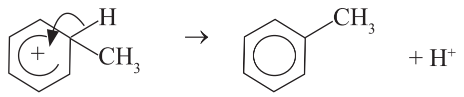
The electrophile involved is a carbocation.
Initially the carbocation electrophile is formed by reaction between the haloalkane and the aluminium chloride catalyst.

$$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + {}^+CH_3$$

The carbocation then combines with benzene to form a second positively charged intermediate.

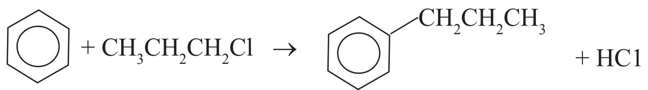


This intermediate then loses a proton to form the alkyl benzene and the proton reacts with $AlCl_4^-$ to reform the catalyst and release hydrogen chloride gas.



$$\text{then } AlCl_4^- + H^+ \rightarrow AlCl_3 + HC1$$

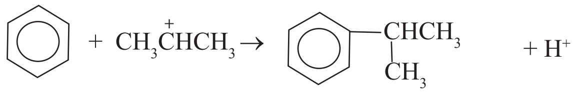
The relative stabilities of carbocations also influences the major product in Friedel-Crafts alkylations. If 1-chloropropane is reacted with benzene, 1-phenylpropane would be the expected product.



However, during the course of the reaction, a significant proportion of the 1-propyl carbocation intermediate *rearranges* to form the more stable 2-propyl carbocation.

$$CH_3CH_2\overset{+}{C}H_2 \rightarrow CH_3\overset{+}{C}HCH_3$$

This carbocation then reacts with benzene to form a significant proportion of 2- phenylpropane, as well as the expected 1-phenylpropane.

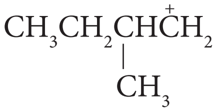
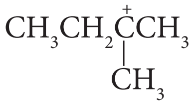
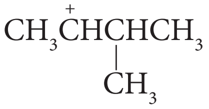
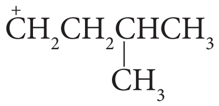
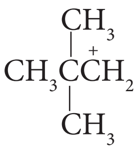


Questions

1. Draw all the possible structures of carbocations with general formula $C_5H_{11}^+$. Classify them as primary, secondary or tertiary.
2. Explaining your answer, deduce the major and minor products when hydrogen bromide reacts with methylpropene.
3. Explain why the reaction between pent-2-ene and hydrogen chloride produces two products in approximately equal proportions rather than one major and one minor product.
4. Explain why the mass spectrum of 2-chloropropane produces a significant peak at m:z 43 whereas 1-chloropropane does not.
5. When 2-bromo-2-phenylbutane undergoes nucleophilic substitution with aqueous sodium hydroxide two isomeric products result. Explain.
6. Benzene is reacted with 1-chlorobutane in the presence of an anhydrous aluminium chloride catalyst. Give the structures of the three mono-substitution products and predict which will predominate. Explain your prediction.

Answers to questions

1.

$CH_3CH_2CH_2CH_2\overset{+}{C}H_2$	Primary	$CH_3CH_2CH_2\overset{+}{C}HCH_3$	Secondary
$CH_3CH_2\overset{+}{C}HCH_2CH_2$	Secondary	 $CH_3CH_2\underset{\substack{\mid\\CH_3}}{C}H\overset{+}{C}H_2$	Primary
 $CH_3CH_2\underset{\substack{\mid\\CH_3}}{\overset{+}{C}}CH_3$	Tertiary	 $CH_3\overset{+}{C}H\underset{\substack{\mid\\CH_3}}{C}HCH_3$	Secondary
 $\overset{+}{C}H_2CH_2\underset{\substack{\mid\\CH_3}}{C}HCH_3$	Primary	 $CH_3\underset{\substack{\mid\\CH_3}}{\overset{\substack{CH_3\\\mid}}{C}}\overset{+}{C}H_2$	Primary

2. Methylpropene [$(CH_3)_2C{=}CH_2$] reacts to form two possible carbocations. These are the more stable tertiary $(CH_3)_2C^+\text{-}CH_3$ and the less stable primary $(CH_3)_2CH\text{-}CH_2^+$. Hence, the major product will be 2-bromo-2-methylpropane [$(CH_3)_2CBr\text{-}CH_3$] formed from the tertiary carbocation and the minor product will be 1-bromo-2-methylpropane [$(CH_3)_2CHCH_2Br$] formed from the primary carbocation.

3. Pent-2-ene [($CH_3CH_2CH{=}CHCH_3$] reacts to form two possible carbocations. These are [($CH_3CH_2CH_2CH^+CH_3$] and [($CH_3CH_2CH^+CH_2CH_3$] which are *both* secondary carbocations and approximately equally stable. They are therefore equally likely to form. Consequently 2-chloropentane [($CH_3CH_2CH_2CHClCH_3$] and 3-chloropentane [($CH_3CH_2CHClCH_2CH_3$] are formed in equal amounts.

4. Both can produce a $[C_3H_7]^+$ carbocation fragment from the respective molecular radical ions. $[C_3H_7Cl]^{+\bullet} \rightarrow [C_3H_7]^+ + {}^\bullet Cl$

   For 2-chloropropane this is a secondary carbocation [$CH_3CH^+CH_3$] which is more stable and therefore more likely to remain intact and be detected in higher proportions. However, for 1-chloropropane this is a primary carbocation [$CH_3CH_2CH_2^+$] which is less stable and therefore less likely to remain intact and will be detected in low proportions.

5. $CH_3CBr(C_6H_5)CH_2CH_3$ ionises to produce a planar, tertiary carbocation [$CH_3C^+(C_6H_5)CH_2CH_3$]. This can be attacked by the hydroxide nucleophile from above or below the plane with equal probability, resulting in a racemic mixture containing the two optical isomers of $CH_3CH(OH)(C_6H_5)CH_2CH_3$.

6. 1-Chlorobutane reacts with $AlCl_3$ to form the less stable primary carbocation, $CH_3CH_2CH_2CH_2^+$. Some of these ions will rearrange to form the more stable secondary and tertiary carbocations $CH_3CH_2CH^+CH_3$ and $(CH_3)_3C^+$. This mixture of three different carbocations (electrophiles) react with benzene to give a mixture of 1-phenylbutane [$C_6H_5CH_2CH_2CH_2CH_3$], 2-phenylbutane [$C_6H_5CH(CH_3)CH_2CH_3$] and 2-methyl-2-phenylpropane [$C_6H_5C(CH_3)_3$].

Acknowledgements: *This Factsheet was researched and written by Mike Hughes.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU.***
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