



CAMBRIDGE
UNIVERSITY PRESS

Chemistry

For the IB Diploma

> Chapter 22

Electron-pair sharing reactions

> Nucleophilic substitution reactions

Primary halogenoalkanes

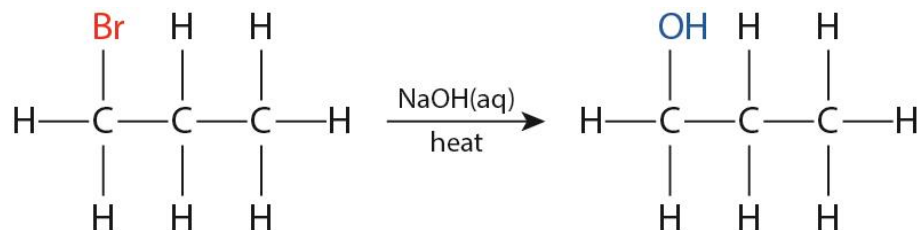
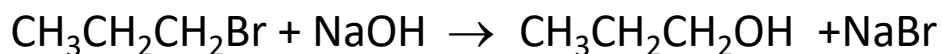


Figure 22.1: A nucleophilic substitution reaction. This sort of diagram is often called a reaction scheme and is used in organic chemistry to show how one organic molecule is converted into another; it is not a balanced equation but just focuses on the organic compounds. Reagents and conditions are usually shown on the reaction arrow.

The balanced equation for this reaction is:



or, as an ionic equation: $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Br}^-$

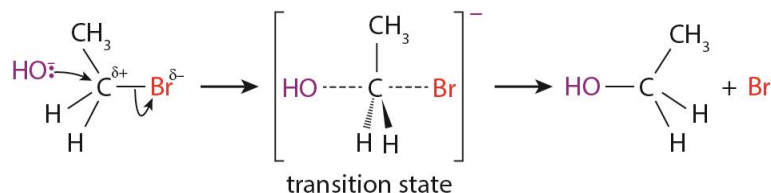


Figure 22.2: The S_N2 mechanism showing the transition state (activated complex).

> Nucleophilic substitution reactions

Tertiary halogenoalkanes

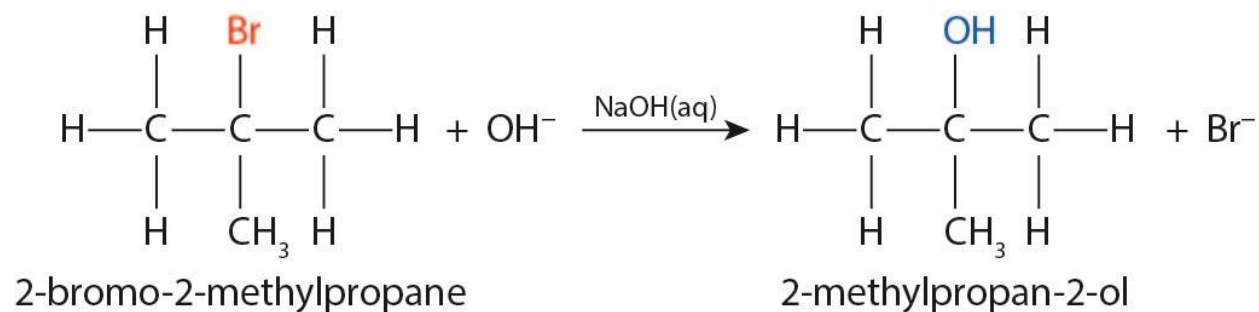


Figure 22.3: A nucleophilic substitution reaction.

> Definitions

Heterolytic fission: a covalent bond breaks so that both electrons go to the same atom.

Nucleophile: a molecule or a negatively charged ion, possessing a lone pair of electrons, which is attracted to a more positively charged region in a molecule (region with lower electron density) and donates a lone pair of electrons to form a covalent (coordination) bond. A nucleophile is a Lewis base.

Substitution reaction: a reaction in which one atom or group is replaced by another atom or group.

Addition reaction: in organic chemistry, a reaction in which a molecule is added to a compound containing a multiple bond without the loss of any other groups.

Electrophile: a reagent (a positively charged ion or the positive end of a dipole) that is attracted to regions of high electron density and accepts a pair of electrons to form a covalent bond. An electrophile is a Lewis acid.

Carbocation: an organic molecular species with a positive charge on a carbon atom.

> Electrophilic addition reactions of alkenes

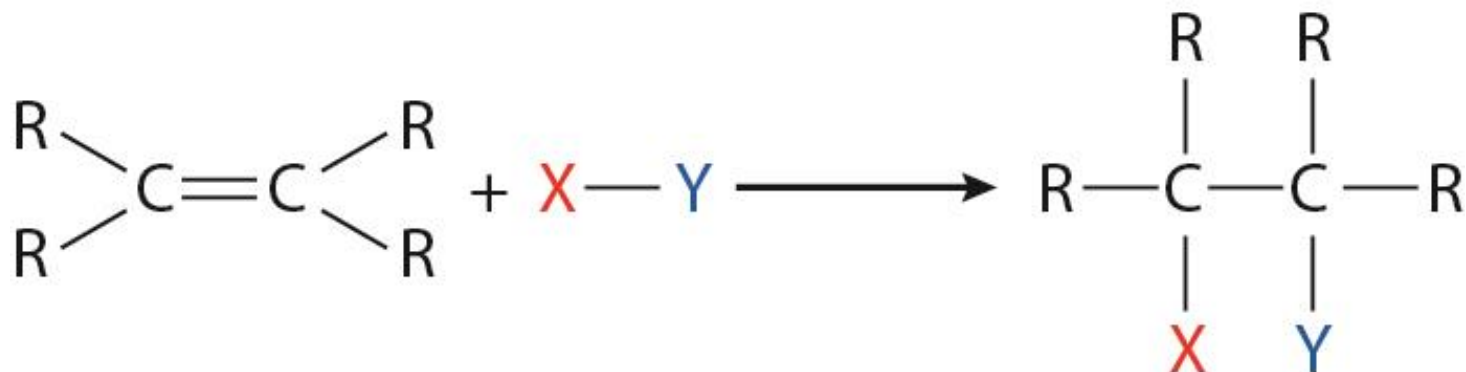


Figure 22.6: Addition reaction of alkenes.

> Definitions

A **Lewis acid** is an electron-pair acceptor.

A **Lewis base** is an electron-pair donor.

In organic chemistry:

A **nucleophile** is a Lewis base and an **electrophile** is a Lewis acid.

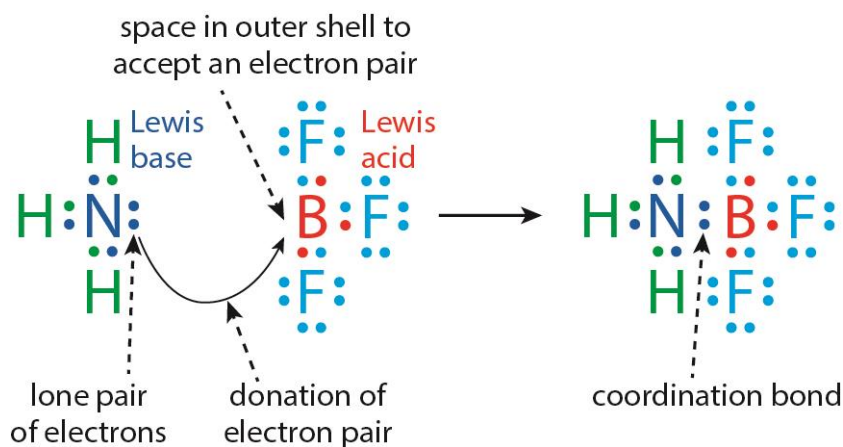


Figure 22.4: Gilbert Lewis

Figure 22.5: An adduct is formed when NH_3 and BF_3 react together. An adduct is formed when two molecular entities join together with the formation of a covalent bond.

➤ Complex ion formation – another example of a Lewis acid–base reaction

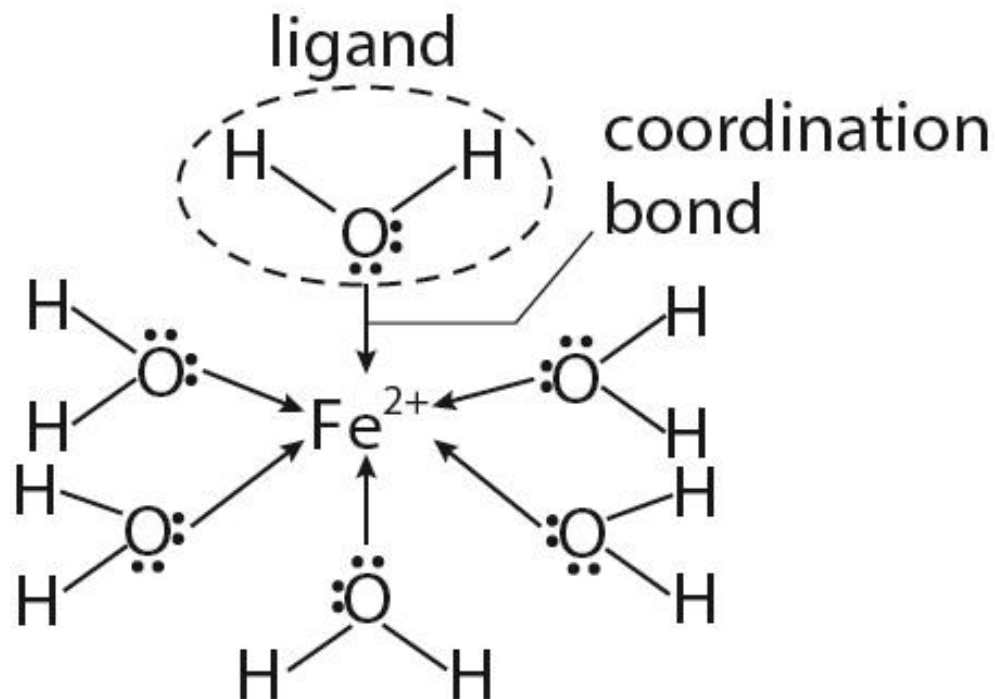


Figure 22.7: A transition element complex ion.

➤ Work out the overall charge of the following complex ions

	Oxidation state of transition metal	Overall charge
$\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2$	+2	
$\text{Mn}(\text{H}_2\text{O})_5\text{OH}$	+3	
$\text{Co}(\text{NH}_3)_3\text{Cl}_3$	+3	

> Nucleophilic substitution reactions for primary halogenoalkanes



Figure 22.8: The S_N2 mechanism showing the transition state (activated complex).

For **primary** halogenoalkanes, the dominant mechanism is S_N2.

> S_N1 mechanism for tertiary halogenoalkanes

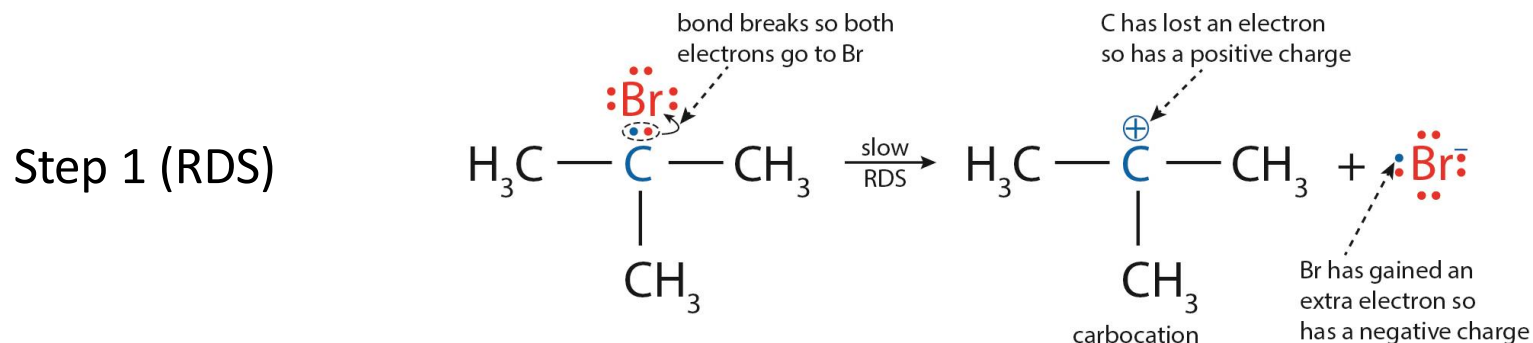


Figure 22.9: An intermediate species is formed. RDS is rate-determining step.

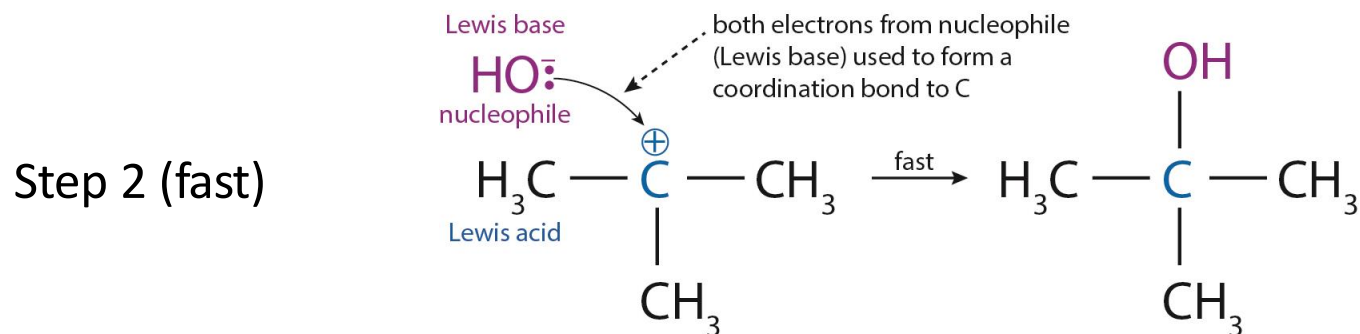


Figure 22.10: The second step of the S_N1 mechanism.

For **tertiary** halogenoalkanes, the dominant mechanism is S_N1.

> The effect of the halogen (leaving group) on the rate of nucleophilic substitution



weaker bond = faster reaction

Bond	Bond energy /kJ mol ⁻¹
C-F	484
C-Cl	338
C-Br	276
C-I	238

> Electrophilic addition

ethene + hydrogen bromide

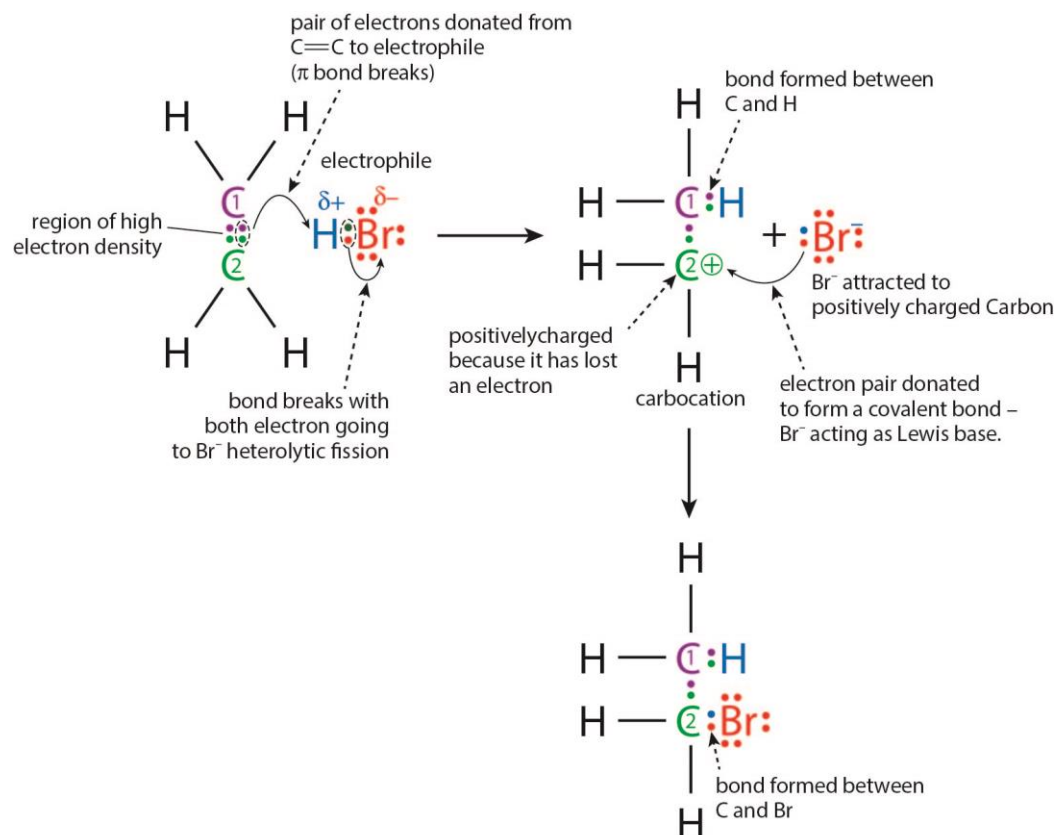


Figure 22.11: The mechanism of the reaction of ethene with hydrogen bromide showing electrons.

> Markovnikov's rule

When an acid, HX, adds across the double bond of an alkene, the H atom becomes attached to the C atom that has the larger number of H atoms already attached.

propene + HBr

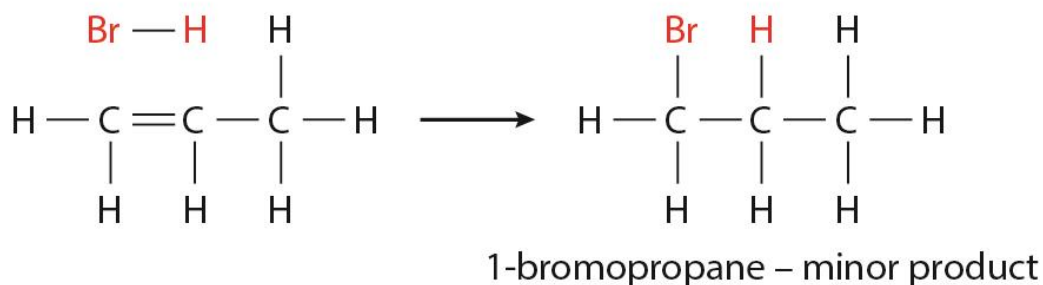
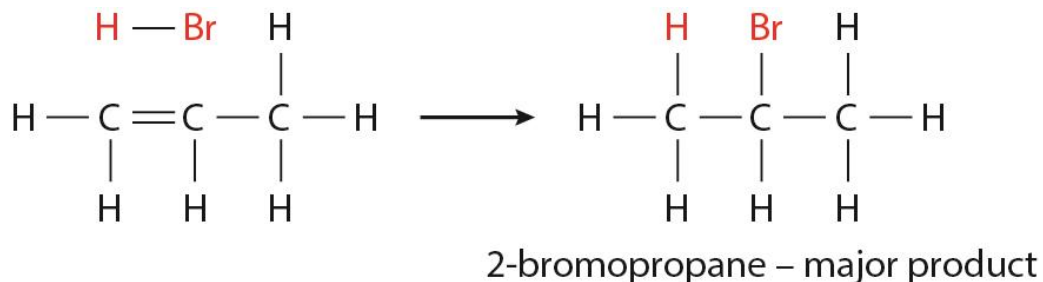


Figure 22.12: Addition of hydrogen bromide to propene results in the formation of two different products.

➤ Stability of the carbocation intermediates

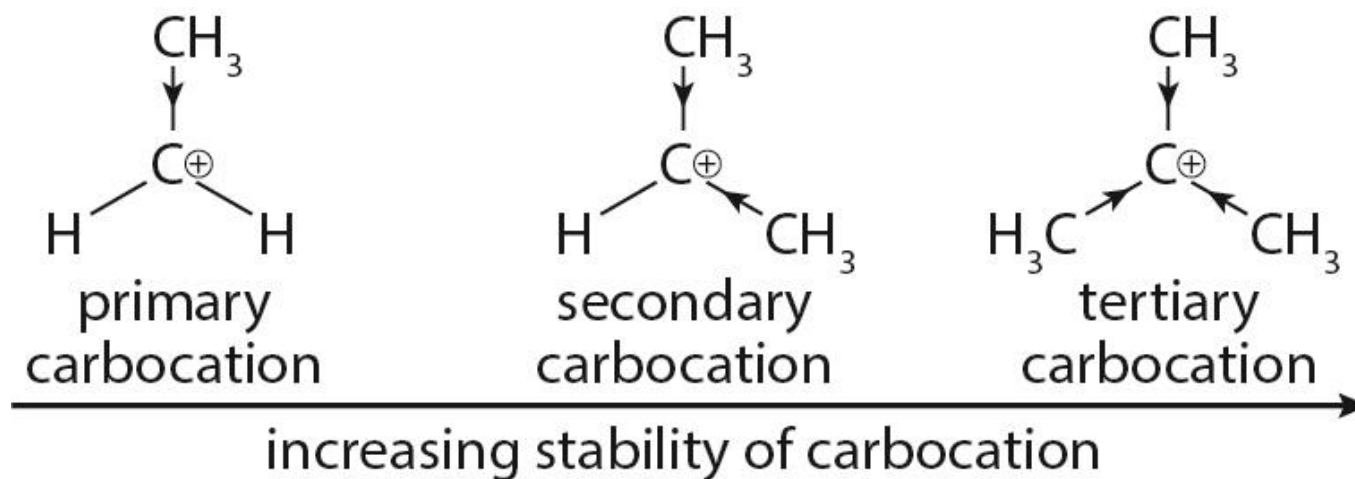
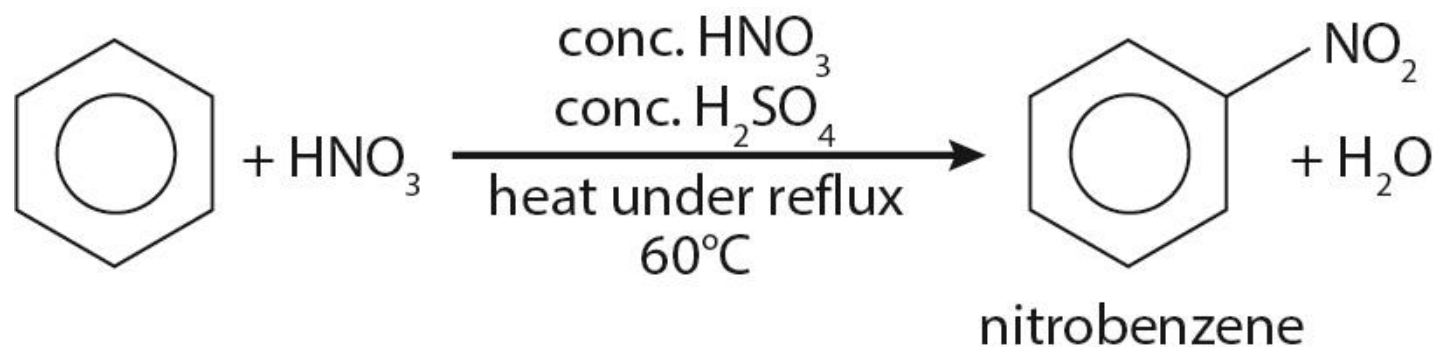


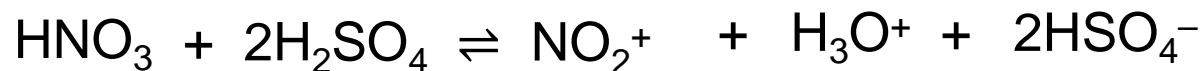
Figure 22.13: Relative stability of carbocations.

> Electrophilic substitution reactions

The nitration of benzene



Formation of the electrophile



> General mechanism for electrophilic substitution on benzene rings



Figure 22.14: The mechanism for electrophilic substitution.