Chem Factsheet

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Oxidation and Reduction in Organic Chemistry

To succeed in this topic you need to understand:
- homologous series (covered in Factsheet 15);
- functional groups (covered in Factsheet 15);
- structural (including displayed) formulae (Factsheet 15);
- naming organic molecules by I.U.P.A.C. rules (Factsheet 15);
- the basic definitions of oxidation and reduction (Factsheet 11);
- the term “redox reaction” (Factsheet 11);
- the terms “oxidant” (oxidising agent) and “reductant” (reducing agent) (Factsheet 11);
- oxidation states / numbers for defining oxidation and reduction (Factsheet 11)

After working through this Factsheet you will be able to:
- recognise reactions of organic molecules as either oxidation or reduction;
- state the reagents and conditions used to achieve a particular oxidation or reduction reaction;
- predict the oxidation and / or reduction products given a particular starting material.

Introduction

The usual definitions for reduction and oxidation are “gain of electrons” and “loss of electrons” respectively. For *organic* redox reactions, although these definitions are still applicable, it is *usually* easier to recognise them in terms of loss or gain of hydrogen or oxygen.

> Oxidation = gain of oxygen or loss of hydrogen
> Reduction = gain of hydrogen or loss of oxygen

Thus, if the structures of the starting material and the product are clearly drawn, applying these definitions will lead to an easy classification by simply noting the changes in structure in terms of addition or loss of either oxygen or hydrogen.

e.g.1 CH_3CH_2OH (ethanol) → CH_3CHO (ethanal)
is an *oxidation* because *2H atoms are removed.*

e.g.2 CH_3CHO (ethanal) → CH_3COOH (ethanoic acid)
is an *oxidation* because *one O atom is added.*

e.g.3 $CH_2{=}CH_2$ (ethene) → CH_3CH_3 (ethane)
is a *reduction* because *2H atoms are added.*

This is commonly applied in simplified equations used to represent the organic redox reactions.

[O] represents the oxygen being added or the agent responsible for removing hydrogen. For example

$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$

$CH_3CHO + [O] \rightarrow CH_3COOH$

Similarly, [H] represents the hydrogen being added or the agent responsible for removing oxygen. For example

$CH_3COOH + 2[H] \rightarrow CH_3CHO + H_2O$

$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$

> **Note:** Water is always formed if *removal* of hydrogen or oxygen occurs

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Having decided that an organic conversion involves either oxidation or reduction, the next problem is to make an appropriate choice of oxidising agent (oxidant) or reducing agent (reductant). The most common reagents you are likely to meet in A-level chemistry are summarised in Table 1.

Table 1. Common Oxidants and Reductants

Oxidants	**Reductants**
Acidified (H_2SO_4) potassium dichromate ($K_2Cr_2O_7$)	Hydrogen (H_2) with nickel catalyst
Alkaline (NaOH) potassium manganate(VII) ($KMnO_4$)	Hydrogen (H_2) with platinum catalyst
Fehling’s solution – alkaline (NaOH) copper sulphate ($CuSO_4$)	Hydrogen (H_2) with palladium catalyst
Tollen’s reagent – alkaline (NH_3) silver nitrate solution ($AgNO_3$)	Lithium aluminium hydride ($LiAlH_4$) in dry ether
Atmospheric oxygen	Sodium borohydride ($NaBH_4$) in aqueous solution
	Tin and hydrochloric acid

Finally you need to know of specific experimental conditions (e.g. temperature, reflux etc.) that are needed to achieve an efficient conversion.

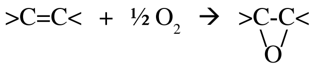
> **Note:** All organic compounds are *combustible* in the presence of oxygen and such reactions can be classified as *oxidations* of these organic molecules. However, even though these reactions are vitally important in providing usable energy but, at the same time, adding to pollution and global warming, they are not of much interest in organic synthesis because combustion invariably destroys the carbon skeleton and functionality of the molecule.

The common, *synthetically-useful* oxidation and reduction reactions can now be summarized.

Functional Group	**Oxidation?**	**Reduction?**	**Functional Group**	**Oxidation?**	**Reduction?**
Alkane	No	No	Carboxylic acid	No	Yes
Alkene	Yes	Yes	Amine	No	No
Alkyne	No	Yes	Amide	No	Yes
Halogenoalkane	No	Yes	Nitrile	No	Yes
Primary alcohol	Yes	No	Arene	Yes	Yes
Secondary alcohol	Yes	No	Acyl chloride	No	Yes
Tertiary alcohol	No	No	Acid anhydride	No	Yes
Aldehyde	Yes	Yes	Ester	No	Yes
Ketone	No	Yes	Nitro compounds	No	Yes

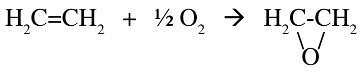
Oxidation of Alkenes

1. By atmospheric oxygen in the presence of a silver catalyst at around 200°C to produce epoxyalkanes



$$>C=C< + \frac{1}{2}O_2 \rightarrow >\underset{O}{C-C}<$$

e.g. Ethene will convert to epoxyethane

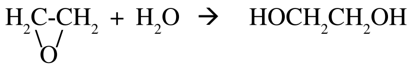


$$H_2C=CH_2 + \frac{1}{2}O_2 \rightarrow \underset{O}{H_2C-CH_2}$$

2. By heating with alkaline potassium manganate(VII) to produce diols $>C=C< + [O] + H_2O \rightarrow >COH\text{-}COH<$

e.g. Propene will convert to propan-1,2-diol
$CH_3CH=CH_2 + [O] + H_2O \rightarrow CH_3CH(OH)\text{-}CH_2OH$

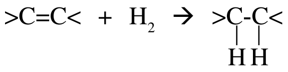
Note: Since this diol is both a primary and a secondary alcohol it can oxidize further to a ketone and carboxylic acid. The diol is best made by producing the epoxyalkane as described in reaction 1, followed by hydration.
e.g. To make ethan-1,2-diol, prepare epoxyethane as described and then react with dilute sulphuric acid at 60°C



$$\underset{O}{H_2C-CH_2} + H_2O \rightarrow HOCH_2CH_2OH$$

Reduction of Alkenes

By hydrogen in the presence of a finely divided nickel catalyst at 150°C to produce alkanes.



$$>C=C< + H_2 \rightarrow >\underset{H}{C}-\underset{H}{C}<$$

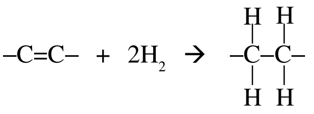
e.g. Propene will convert to propane
$CH_3CH=CH_2 + H_2 \rightarrow CH_3CH_2CH_3$

Note: this reaction is of particular significance in the *hydrogenation* of vegetable oils to produce soft margarines.

Note: other catalysts (Pt, Pd) can be used but nickel is preferred in most cases because of its lower cost.

Reduction of Alkynes

By hydrogen in the presence of a finely divided nickel catalyst at 150°C to produce alkanes.



$$-C=C- + 2H_2 \rightarrow -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$$

e.g. Ethyne will convert to ethane
$CH=CH + 2H_2 \rightarrow CH_3CH_3$

Note: this reaction is exactly parallel to that of alkenes because both involve hydrogenation of unsaturated carbon-to-carbon bonds.

Reduction of Halogenoalkanes

By refluxing with lithium aluminium hydride in dry ether followed by acidification to produce the corresponding alkane

$C–Cl + 2[H] \rightarrow C–H + HCl$

e.g. Bromomethane will convert to methane
$CH_3Br + 2[H] \rightarrow CH_4 + HBr$

Oxidation of Primary Alcohols

By heating with acidified (H_2SO_4) potassium dichromate solution to produce aldehydes (–CHO) and carboxylic acids (–COOH).

$–CH_2OH + [O] \rightarrow –CHO + H_2O$
then $–CHO + [O] \rightarrow –COOH$

e.g. Butan-1-ol will convert to butanal and then butanoic acid
$CH_3CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2CHO + H_2O$
then $CH_3CH_2CH_2CHO + [O] \rightarrow CH_3CH_2CH_2COOH$

Note: The yield of aldehyde rather than acid can be maximized by reducing the time the alcohol is in contact with the oxidant and avoiding an excess of oxidant. These are achieved by immediate distillation of the reaction mixture and adding the oxidant to the alcohol in small controlled amounts *during* the course of the reaction. Conversely, acid production is maximized by refluxing the reaction mixture and using excess oxidant right from the start.

Oxidation of Secondary Alcohols

By heating with acidified (H_2SO_4) potassium dichromate solution to produce ketones

(C–CO–C). $C–CHOH–C + [O] \rightarrow C–CO–C + H_2O$

then $–CHO + [O] \rightarrow –COOH$

e.g. Propan-2-ol will convert to propanone
$CH_3CHOHCH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$

Note: Reflux is the standard technique here because ketones do not oxidize further.

Oxidation of Tertiary Alcohols

None

Note: No easy oxidation because tertiary alcohols do not contain the –CHOH – group seen in both primary and secondary alcohols. Both H atoms are needed for oxidation to C=O to occur.

Note: This can be used as a test to distinguish tertiary alcohols from primary and secondary alcohols. When heated with orange acidified dichromate, tertiary alcohols will have ***no effect*** on this colour but primary and secondary alcohols will cause an ***orange to green*** colour change.

Note: Vigorous oxidation by potassium manganate(VII) causes the carbon chain to break down. This is not synthetically useful.

Oxidation of Aldehydes

By heating with acidified (H_2SO_4) potassium dichromate solution to produce carboxylic acids

(–COOH). $–CHO + [O] \rightarrow –COOH$

e.g. Ethanal will convert to ethanoic acid
$CH_3CHO + [O] \rightarrow CH_3COOH$

Note: This is related to Tollen's test (ammoniacal silver nitrate solution) and Fehling's test (alkaline copper(II) sulphate). These are used as tests to distinguish aldehydes from ketones. The emphasis is given to the visible reduction of Ag^+ to Ag (mirror) or Cu^{2+} to Cu^+ (red precipitate) by an aldehyde but not a ketone. But don't forget when the metal ions are reduced something, in this case an aldehyde, has to be oxidized

Reduction of Aldehydes

By refluxing with lithium aluminium hydride in dry ether or sodium borohydride in aqueous solution followed by acidification to produce the corresponding primary alcohol.

$–CHO + 2[H] \rightarrow –CH_2OH$

e.g. Propanal will convert to propan-1-ol
$CH_3CH_2CHO + 2[H] \rightarrow CH_3CH_2CH_2OH$

Reduction of Carboxylic Acids

By refluxing with lithium aluminium hydride in dry ether followed by acidification to produce the corresponding primary alcohol.

$–COOH + 4[H] \rightarrow –CH_2OH + H_2O$

e.g. Ethanoic will convert to ethanol
$CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$

Note: Acids are reduced by $LiAlH_4$ but not by $NaBH_4$. Aldehydes and ketones are reduced by both.

Reduction of Ketones

By refluxing with lithium aluminium hydride in dry ether or sodium borohydride in aqueous solution followed by acidification to produce the corresponding secondary alcohol.

$C–CO–C + 2[H] \rightarrow C–CH(OH)–C$

e.g. Butan-2-one will convert to butan-2-ol
$CH_3CH_2COCH_3 + 2[H] \rightarrow CH_3CH_2CH(OH)CH_3$

Note: The fact that ketones are not easily oxidized means that, unlike aldehydes, they are not reducing agents. This is used to distinguish aldehydes from ketones. These tests were discussed earlier.

Reduction of Amides

By refluxing with lithium aluminium hydride in dry ether followed by acidification to produce the corresponding primary amine.

$–CONH_2 + 2[H] \rightarrow –CH_2NH_2$

e.g. Ethanamide will convert to aminoethane
$CH_3CONH_2 + 2[H] \rightarrow CH_3CH_2NH_2$

Reduction of Nitro Compounds

By refluxing with granulated tin or iron filings and concentrated hydrochloric acid, followed by addition of sodium hydroxide to produce the corresponding primary amine.

$C–NO_2 + 6[H] \rightarrow C–NH_2 + 2H_2O$

e.g. Nitrobenzene converts to aminobenzene
$C_6H_5–NO_2 + 6[H] \rightarrow C_6H_5–NH_2 + 2H_2O$

Reduction of Nitriles

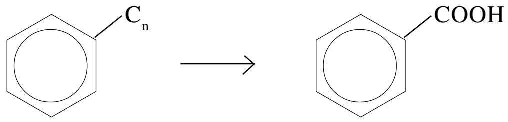
By refluxing with lithium aluminium hydride in dry ether followed by acidification to produce the corresponding primary amine.

$–C{\equiv}N + 4[H] \rightarrow –CH_2NH_2$

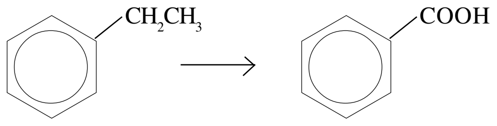
e.g. Propanamide will convert to 1-aminopropane
$CH_3CH_2CN + 2[H] \rightarrow CH_3CH_2CH_2NH_2$

Oxidation of Arenes

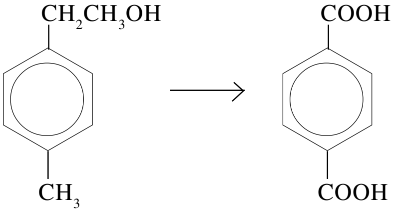
The benzene ring structure is very stable and not easily oxidized. However, *any* carbon-based side-chains are oxidized to –COOH when arenes are refluxed with alkaline potassium manganate(VII).



e.g. Ethyl benzene converts to benzoic acid



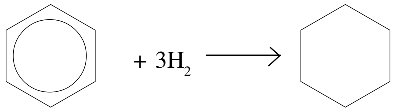
e.g. 2-(4-methylphenyl)-ethanol converts to benzene-1,4-dicarboxylic acid



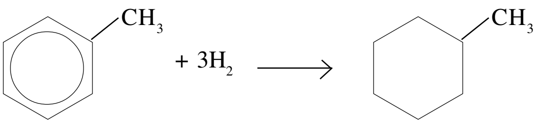
Note: Writing balanced equations here is difficult because so many other products are formed. Most significantly, the remaining C atoms from each side-chain are converted to CO_2.

Reduction of Arenes

Benzene rings and related aromatic structures are reduced by hydrogen in the presence a nickel catalyst at 150°C to produce the corresponding cycloalkanes.



e.g. Methylbenzene converts to methylcyclohexane



Additional Points:

1. Remember to classify any given reaction in terms of loss or gain of oxygen or hydrogen before attempting to select appropriate reagents and reaction conditions.

2. Be aware that more than one functional group may be oxidized or reduced.

   e.g. 1 Propan-1,2-diol has two alcohol groups, one primary and one secondary. Under prolonged oxidation these will convert to ketone and carboxylic acid groups respectively.

   $CH_3CH(OH)CH_2OH + 3[O] \rightarrow CH_3COCOOH + 2H_2O$

   e.g.2 Phenyl ethene has a benzene ring and an alkene group. When reacted with hydrogen and a nickel catalyst at 150°C it will covert to ethylbenzene.

   Related to this is the idea of *selective oxidation or reduction*. This will not concern you at A-level but, by choice of an appropriate oxidant or reductant it is possible to reduce one group and not another. In fact, this applied to an earlier example where nitrobenzene is reduced to amino benzene using tin and hydrochloric acid. Note that the NO_2 group is reduced but the benzene ring is not.

   In this context, look back at the point about $NaBH_4$ compared to $LiAlH_4$ made earlier!

3. Acid derivatives such as acyl chlorides, acid anhydrides and esters undergo *reductive hydrolysis* with lithium aluminium in dry ether. This means they are hydrolysed to the corresponding acid which is then reduced to the corresponding primary alcohol.

   e.g. $CH_3COCl \rightarrow CH_3COOH \rightarrow CH_3CH_2OH$

   $(CH_3CO)_2O \rightarrow 2CH_3COOH \rightarrow 2CH_3CH_2OH$

   $CH_3COOCH_3 \rightarrow CH_3COOH + CH_3OH \rightarrow CH_3CH_2OH + CH_3OH$

4. Simultaneous oxidation and reduction of the same organic molecule is also possible. This is called *disproportionation*. The best example is the disproportionation of two aldehyde groups to a primary alcohol and a carboxylic acid. In effect, one aldehyde group oxidizes the other and so becomes reduced itself.

   These are specialized reactions which you probably would not be expected to "know" but you can now use the principles of this Factsheet to recognize them!

   e.g. $2C_6H_5CHO + H_2O \rightarrow C_6H_5CH_2OH + C_6H_5COOH$

   This is achieved by heating the aldehyde with potassium hydroxide solution.

Practice Questions

1. Classify each of the following as oxidation, reduction, disproportionation or not redox
   (a) $CH_3OH \rightarrow HCHO$
   (b) $C_6H_5CH_2CH_2CH_2COOH \rightarrow C_6H_5COOH$
   (c) $CH_3CH_2CN \rightarrow CH_3CH_2CH_2NH_2$
   (d) $CH_3COOH \rightarrow CH_3COCl$
   (e) Cyclohexanol → cyclohexanone
   (f) $C_6H_5CHO \rightarrow C_6H_{11}CH_2OH$
   (g) $CH_3CHO \rightarrow CH_3CH_2OH + CH_3COOH$
   (h) $CH_3COCH_2CH_3 \rightarrow CH_3CH(OH)CH_2CH_3$
   (i) $CH_3CH_2Br \rightarrow CH_3CH_2OH$
   (k) $CH_3COCH_2COCH_3 \rightarrow CH_3CH(OH)CH_2CH(OH)CH_3$

2. Explaining your choice, classify each of the following as oxidation or reduction and then write an appropriate equation for the conversion described. Use [O] and [H] where appropriate.
   (a) $CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3$
   (b) $CH_3CH_2CH_2NO_2 \rightarrow CH_3CH_2CH_2NH_2$
   (c) $C_6H_5CHO \rightarrow C_6H_{11}CH_2OH$
   (d) $C_6H_5CH_2CH_2OH \rightarrow C_6H_5CH_2COOH$
   (e) $CH_3COCH_2COCH_3 \rightarrow CH_3CH(OH)CH_2CH(OH)CH_3$

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3. Explaining your choice, classify each of the following as oxidation or reduction and then select reagents and conditions to achieve the conversion described
   (a) $C_6H_5CHO \rightarrow C_6H_{11}CH_2OH$
   (b) $CH_3CH_2CONH_2 \rightarrow CH_3CH_2CH_2NH_2$
   (c) $C_6H_5CH(OH)CH_2CH_3 \rightarrow C_6H_5COCH_2CH_3$
   (d) $C_6H_5CH_2CH_2CH_2CHO \rightarrow C_6H_5COOH$
   (e) $CH_3COCH_2COCH_2COCH_3 \rightarrow CH_3CH(OH)CH_2CH(OH)CH_2CH(OH)CH_3$

4. Alcohols react with acidified dichromate(VI) solution in various ways depending on the type of alcohol used and the reaction conditions and method. Describe the results of each of the following reactions, giving the names and structures of the products where appropriate.
   (a) Butan-1-ol is refluxed with excess acidified sodium dichromate(VI).
   (b) Butan-2-ol is refluxed with excess acidified sodium dichromate(VI).
   (c) Butan-1-ol is heated and distilled whilst acidified sodium dichromate(VI) is added slowly.
   (d) 2-Methylpropan-2-ol is boiled under reflux with excess acidified sodium dichromate(VI).
   (e) With reference to (c), explain why the sodium dichromate(VI) is added to butan-1-ol (rather than the other way round) and why it is possible to distil out the product as it is formed.

5. Aldehydes and ketones can both be reduced to alcohols by lithium aluminium hydride, $LiAlH_4$.
   (a) State the conditions under which this reagent is used.
   $X = CH_3CH(OH)COOH$ $Y = CH_3COCOOH$
   X may be produced from Y by reduction, but this cannot be achieved using lithium aluminium hydride
   (b) Give the name and structure of the product if this reagent is used?
   (c) How would you obtain X from Y?

Answers

1. (a) Oxidation (b) Oxidation (c) Reduction (d) Not redox (e) Oxidation (f) Reduction
   (g) Disproportionation (h) Reduction (i) Not redox (k) Reduction

2. (a) Oxidation because H removed: $CH_3CH(OH)CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_3 + H_2O$
   (b) Reduction because H added: $CH_3CH_2CH_2NO_2 + 6[H] \rightarrow CH_3CH_2CH_2NH_2 + 2H_2O$
   (c) Reduction because H added: $C_6H_5CHO + 8[H] \rightarrow C_6H_{11}CH_2OH$
   (d) Oxidation because H removed: $C_6H_5CH_2CH_2OH + 2[O] \rightarrow C_6H_5CH_2COOH + H_2O$
   (e) Reduction because H added: $CH_3COCH_2COCH_3 + 4[H] \rightarrow CH_3CH(OH)CH_2CH(OH)CH_3$

3. (a) Reduction because H is added; aldehyde to primary alcohol and arene to cyclohexane
   $C_6H_5CHO + 8[H] \rightarrow C_6H_{11}CH_2OH$
   Hydrogen gas with nickel catalyst at 150°C.
   Note: Use of lithium aluminium hydride in dry ether would reduce *only* the aldehyde group.
   (b) Reduction because H is added; amide to primary amine
   $CH_3CH_2CONH_2 + 4[H] \rightarrow CH_3CH_2CH_2NH_2$
   Reflux with lithium aluminium hydride in dry ether, followed by aqueous acid. Then add aq NaOH to release the amine
   (c) Oxidation because H removed; secondary alcohol to ketone
   $C_6H_5CH(OH)CH_2CH_3 + [O] \rightarrow C_6H_5COCH_2CH_3 + H_2O$
   Heat under reflux with excess acidified potassium dichromate
   (d) Oxidation with degradation of aryl side-chain.
   $C_6H_5CH_2CH_2CH_2CHO + 10[O] \rightarrow C_6H_5COOH + 3CO_2 + 3H_2O$
   (**Note :** this is a much simplified equation)
   reflux with alkaline potassium permanganate
   (e) Reduction because H is added; trione to triol
   $CH_3COCH_2COCH_2COCH_3 + 6[H] \rightarrow CH_3CH(OH)CH_2CH(OH)CH_2CH(OH)CH_3$
   Reflux with lithium aluminium hydride in dry ether, followed by aqueous acid.

4. (a) This primary alcohol is oxidized to butanoic acid, $CH_3CH_2CH_2COOH$, because the oxidant is in excess and reaction is prolonged. The dichromate mixture will change from orange to green.
   (b) This secondary alcohol is oxidized to butanone, $CH_3CH_2COCH_3$, because the oxidant is in excess and reaction is prolonged. Ketones do not oxidize further. The dichromate mixture will change from orange to green.
   (c) This primary alcohol is oxidized to butanal, $CH_3CH_2CH_2CHO$, because the oxidant is not in excess and the contact time is short. The dichromate mixture will change from orange to green.
   (d) This tertiary alcohol is not oxidized. The dichromate mixture will remain orange.
   (e) To avoid the presence of excess oxidant.
   Aldehydes have much lower boiling points than the corresponding alcohol because alcohol molecules are attracted to each other by stronger inter-molecular forces. Hydrogen bonds exist in alcohols but only dipole-dipole forces in aldehydes.

5. (a) Reflux in dry ether, followed by aqueous acid.
   (b) $CH_3CH(OH)CH_2OH$; propan-1,2-diol
   (c) Use a milder reductant such as sodium borohydride in aqueous solution. This selectively reduces the ketone group.