

Chemistry, WM Revision Notes

Noah Phipps¹

¹Affiliation not available

March 16, 2023

Abstract

Contents

1	WM1	1
1.1	Alcohols	1
1.1.1	Physical Properties of Alcohols	1
1.2	Reactions of Alcohols	1
1.2.1	Types of alcohols	1
1.2.2	Oxidation	1
1.2.3	Heating under Reflux	1
1.2.4	Oxidation of Primary alcohols	2
1.2.5	Oxidation of Secondary alcohols	2
1.2.6	Oxidation of Tertiary alcohols	2
1.2.7	Dehydration of Alcohols	3
1.2.8	Substitutions of Alcohols with Halide ions	3
1.2.9	Esterification of Alcohols	3
1.2.10	Esterification of Alcohols using an Acid Anhydride	4
1.2.11	Ethers	4
2	WM2	5
2.1	Carboxylic Acids	5
2.2	Hydroxyl Group	5
2.2.1	Acidic Properties of Hydroxyl group	5
2.3	Testing for Phenol and derivatives	5
2.4	Ester formation from Phenols and Acid Anhydrides	6
2.5	Esterification of Salicylic Acid	6
2.5.1	Esterification of the <i>OH</i> group	6
2.5.2	Esterification of the <i>COOH</i> group	6
3	WM3	7
3.1	Infrared Spectroscopy	7
3.1.1	Bond Deformation	7
3.1.2	Interpreting Spectra	7
4	WM4	8
4.1	Mass Spectrometry	8
5	WM5	10
5.1	Green Chemistry	10
5.2	Purification Techniques	10
5.2.1	Recrystallisation	10
5.2.2	Thin Layer Chromatography(TLC)	11
5.2.3	Melting Point Determination	11

List of Figures

1	Oxidation of Primary Alcohols	2
2	Oxidation of secondary alcohols	3
3	Esterification of alcohols	3
4	Reactions with Sodium Hydroxide	6
5	Infrared Absorptions in organic molecules	8
6	An example mass spectrum	9
7	Principles of green chemistry	10

List of Tables

1 WM1

1.1 Alcohols

1.1.1 Physical Properties of Alcohols

- Polar due to *O-H* bond
- Able to hydrogen bond
 - Explains why alcohols have higher MBP's than corresponding alkanes
 - Also explains why alcohol and water mix
- *O-H* bond becomes less influential in longer chains
 - Solubility in water decreases
 - Other properties more similar to those of corresponding alkanes

1.2 Reactions of Alcohols

1.2.1 Types of alcohols

Primary alcohols:

- *-O-H* carbon bonded to one other

Secondary alcohols:

- *-O-H* carbon bonded to two others

Tertiary alcohols:

- *-O-H* carbon bonded to three others

1.2.2 Oxidation

- The *O-H* group is oxidised by strong oxidising agents
 - Acidified Potassium Dichromate(VI), $K_2Cr_2O_7$
 - * Orange dichromate ion reduced to green chromate(III) ion
 - * $Cr_2O_7^{2-} \Rightarrow Cr^{3+}$
- *O-H* group converted to carbonyl $C=O$ group
- Will not take place if there is no hydrogen attached to the carbon
- Carbonyl formed depends on reacting alcohol and conditions
 - Aldehyde or ketone

1.2.3 Heating under Reflux

- Safer when using volatile compounds
- Prevents loss of solvent, reagent, or product

1.2.4 Oxidation of Primary alcohols

- Initially oxidised to an Aldehyde
- Can be further oxidised to a Carboxylic Acid
 - Excess oxidising agent
 - Under reflux
- If the Aldehyde is required:
 - Distilled in situ
 - * Prevents further oxidation
 - Excess Alcohol
 - No reflux

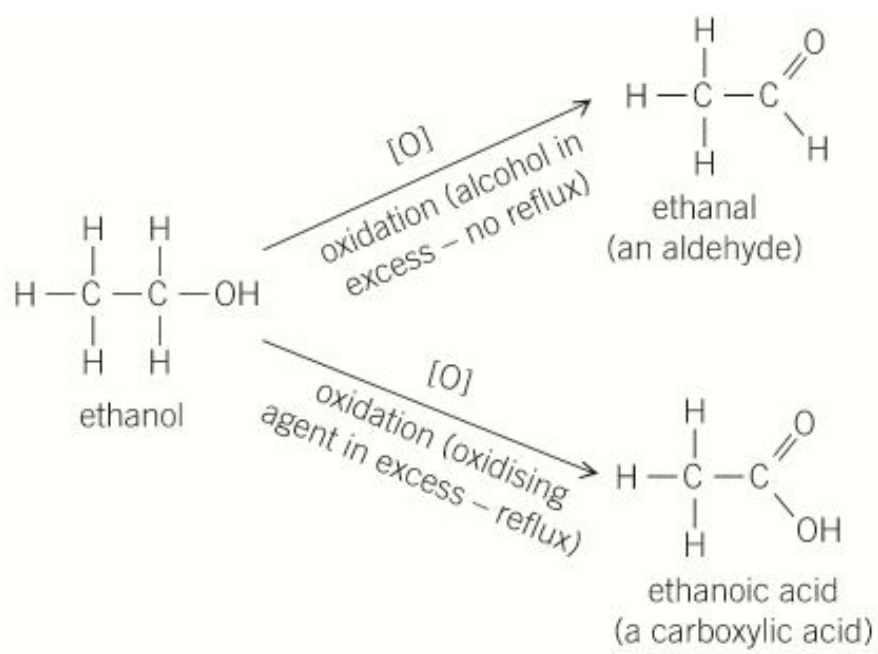


Figure 1: Oxidation of Primary Alcohols

1.2.5 Oxidation of Secondary alcohols

- Oxidised to ketones
 - Excess oxidising agent
 - Under reflux
- No further oxidation
 - Due to strong $\text{C}-\text{C}$ bond

1.2.6 Oxidation of Tertiary alcohols

- Cannot be oxidised

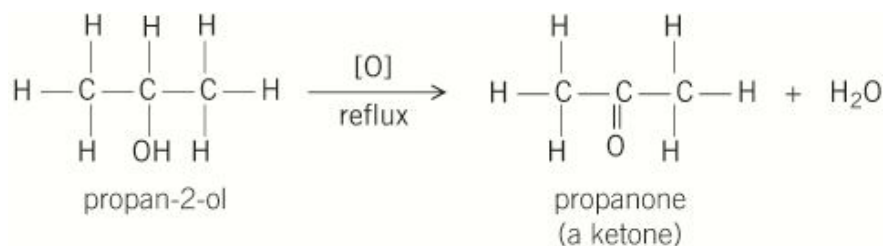


Figure 2: Oxidation of secondary alcohols

1.2.7 Dehydration of Alcohols

- Lose a water molecule to form an Alkene
 - Alumia catalyst
 - 300°C
 - OR
 - Under reflux
 - Concentrated sulfuric acid
- Produces water and corresponding alkene

1.2.8 Substitutions of Alcohols with Halide ions

- Nucleophilic substitution
- In presence of a strong acid
- Gives haloalkane
- H^+ from acid joins with O-H displaced by Halide to form water

1.2.9 Esterification of Alcohols

- An alcohol with a carboxylic acid
- Slow without a strong acid catalyst
 - Concentrated hydrochloric/sulfuric acid
 - Under reflux
- Reversible reaction
 - Ester must be separated and purified

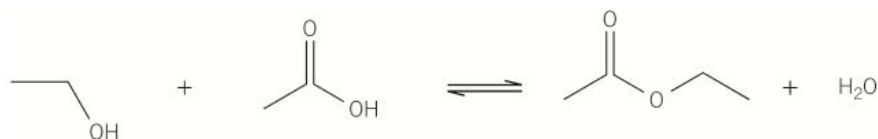
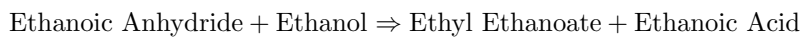


Figure 3: Esterification of alcohols

1.2.10 Esterification of Alcohols using an Acid Anhydride

- Derivatives of carboxylic acids
- Much faster
- Reacts completely on warming
 - Higher yield of ester
- Eg.



1.2.11 Ethers

- -O-
- Structural isomers of alcohols
- Derived from alkanes
 - Substitution of H for -OR, alkoxy group

2 WM2

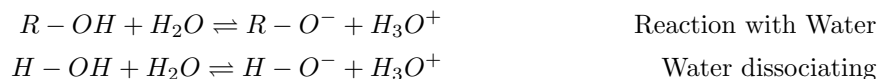
2.1 Caroxylic Acids

- Contain $-COOH$ carboxyl group
- Rest of structure varies
- Can be attached to a benzene ring
- Many derivatives
 - Esters
 - Acid Anhydrides

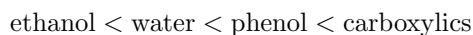
2.2 Hydroxyl Group

- OH
- Presents in 3 ways
 - Carboxyl
 - Alcohol
 - Phenols
 - * Attached to a benzene ring

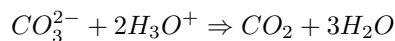
2.2.1 Acidic Properties of Hydroxyl group



The oxonium ion is acidic. The strengths of the acids vary, dependent on how far to the right the equilibrium lies;



- Phenol can react with Sodium Hydroxide to form salts
- Carboxylics can react with Sodium Hydroxide to form salts
- Carboxylics also react with carbonates and fixx



2.3 Testing for Phenol and derivatives

- A purple complex will be formed with Fe^{3+} in a neutral solution
- Iron(III) Chloride

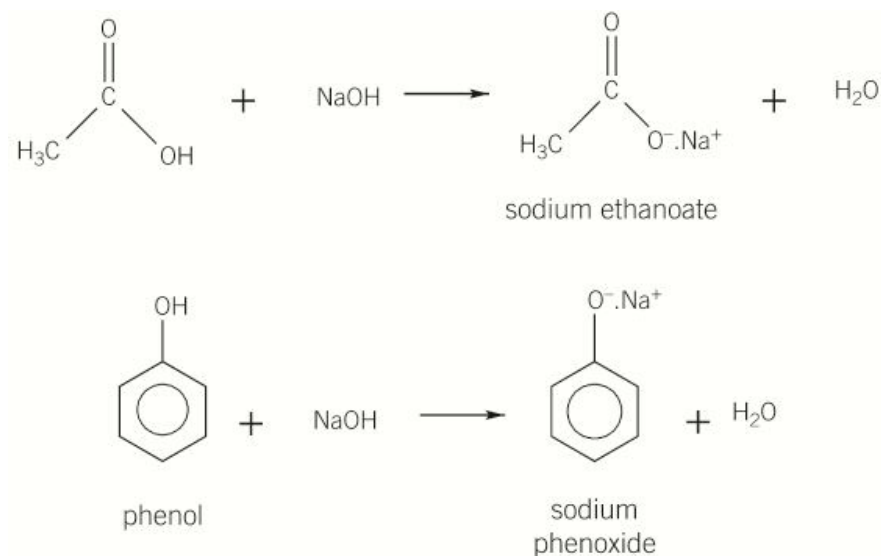
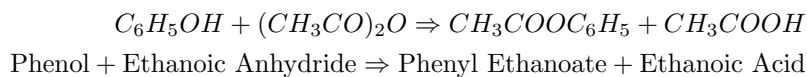


Figure 4: Reactions with Sodium Hydroxide

2.4 Ester formation from Phenols and Acid Anhydrides

- Alkaline conditions



Phenols will **not react** with carboxylic acids to produce esters.

2.5 Esterification of Salicylic Acid

There are two ways to esterify salicylic acid.

2.5.1 Esterification of the *OH* group

- Gives Aspirin
- Esterified with acid anhydride
- Fairly soluble

2.5.2 Esterification of the *COOH* group

- Gives Oil of Wintergreen
 - Methyl-2-hydroxybenzoate
- Esterified with alcohol
- Typically methanol

3 WM3

3.1 Infrared Spectroscopy

- Molecule energies are quantised
- Substance exposed to radiation
 - $10^{13} \rightarrow 10^{14}\text{Hz}$
 - Vibrational energy changes
 - Specific IR frequencies absorbed

$$c = \lambda f$$

- Wavenumber $= \frac{1}{\lambda}\text{cm}^{-1}$

3.1.1 Bond Deformation

- Simple diatomic molecules one vibrate one way
 - Stretching
 - Only one absorption
- More complex molecules vibrate in many different ways

3.1.2 Interpreting Spectra

- Fingerprint region below 1500cm^{-1}
 - Identification by comparison
- Intensity dependent on change in bond polarity
- Hydrogen bonding broadens peaks due to *OH* stretching vibration

Bond	Location	Wavenumber / cm^{-1}	Intensity
C—H	alkanes	2850–2950	M—S
	alkenes, arenes,	3000–3100	M—S
	alkynes	<i>ca</i> 3300	S
C=C	alkenes	1620–1680	M
	arenes	several peaks in range 1450–1650	variable
C≡C	alkynes	2100–2260	M
C=O	aldehydes	1720–1740	S
	ketones	1705–1725	S
	carboxylic acids	1700–1725	S
	esters	1735–1750	S
	amides	1630–1700	M
C—O	alcohols, ethers, esters	1050–1300	S
C≡N	nitriles	2200–2260	M
C—F	fluoroalkanes	1000–1400	S
C—Cl	chloroalkanes	600–800	S
C—Br	bromoalkanes	500–600	S
O—H	alcohols, phenols	3600–3640	S
	*alcohols, phenols	3200–3600	S (broad)
	*carboxylic acids	2500–3200	M (broad)
N—H	primary amines	3300–3500	M—S
	amides	<i>ca</i> 3500	M

* hydrogen-bonded M = medium S = strong

Figure 5: Infrared Absorptions in organic molecules

4 WM4

4.1 Mass Spectrometry

Mass spectrometry is used to find the atomic mass and relative abundances of isotopes in an element.

- Fragmentation pattern
 - Strongest peak calibrated to 100%

- Molecular ion peak may be too low to see
 - * Molecule with only one electron removed, M^+
- Peak at $M + 1$ due to Carbon-13
 - 1.1% of Carbon is Carbon-13
- All molecules and fragments are ionised
 - Must be denoted with charge of +1
- Groups can be conspicuous by absence

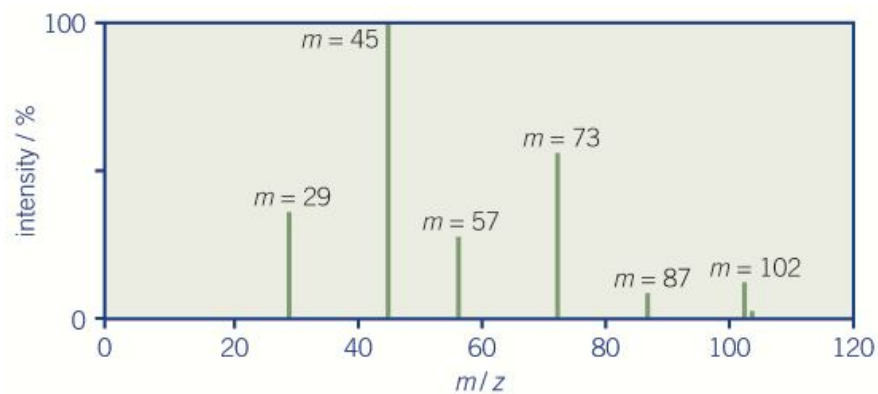


Figure 6: An example mass spectrum

5 WM5

5.1 Green Chemistry

- Green chemistry is developing sustainable and environmentally friendly chemical products and processes
- Does not always correlate with cost
- Processes are often a compromise

Principles	Explanation
Better atom economy	Means more of the feedstock is incorporated into the product and less waste products are produced.
Prevention of waste products	This is better than treating and disposing of waste.
Less hazardous chemical synthesis	Using less hazardous chemicals in the chemical reaction.
Design safer chemical products	Less toxic and hazardous chemical products.
Use safer solvents	Minimise the use of organic solvents.
Lower energy usage	Lower temperature and pressure processes.
Use renewable feedstocks	Instead of depleting natural resources.
Reduce reagents used and the number of steps	As these can generate waste.
Use catalysts and more selective catalysts	These generally reduce energy usage and waste products.
Design chemical products for degradation	When released into the environment should break down into innocuous products.
Employ real time process monitoring	Better monitoring of chemical processes reduces waste products.
Use safer chemical processes	Choose processes that minimise the potential for releasing gases, fires and explosions.

Figure 7: Principles of green chemistry

5.2 Purification Techniques

5.2.1 Recrystallisation

- Purification of solid, crude organic products
- Hot solvent

- Crash cooling
- Filtered, washed, and dried

5.2.2 Thin Layer Chromatography(TLC)

- Separation of small amounts of organic compounds
- Checking purity of samples
- Suitable solvent required
- silica plate is the chromatography medium

5.2.3 Melting Point Determination

- Gives evidence of identity and purity
- Desired compound should melt with $\pm 0.5^{\circ}\text{C}$