A Second Year Blog on Ketones ($R_1R_2>C=O$) where both R_1 and R_2 are Alkyl species

(for the week commencing the 29th of December 2019)

At 'A' Level, most of the required knowledge consists of knowing the difference between Aldehydes and Ketones.

Oxidisation Reactions of Aldehydes (and the accompanying colour changes)

Under **GENTLE** Oxidisation, (I will repeat that, under **GENTLE** Oxidisation)

Primary (i.e. 1˚) Alcohols —> ALDEHYDES, and then ALDEHYDES —> CARBOXYLIC ACIDS.
Secondary (i.e. 2˚) Alcohols —> KETONES.
Tertiary (i.e. 3˚) Alcohols : RESIST GENTLE OXIDISATION.

Tertiary Alcohols are not oxidised under gentle oxidisation therefore there is no colour change. However, with Primary and Secondary Alcohols the oxidisation to an Aldehyde or to a Ketone (respectively) is accompanied by a colour change **from orange to green**.

The oxidisation of an Aldehyde to a Carboxylic Acid

- With acidified Potassium Dichromate and conc. Sulphuric Acid (just warm the mixture)
- With Tollen's reagent: warm freshly prepared $AgNO_3$ and NaOH *in situ* (and, generally speaking, **a silver precipitate will form with an Aldehyde but not with a Ketone**)
- Fehling's and Benedict's reagents (the blue Cu^{2+} ions in the solution are converted into Cu^{1+} ions and the solution turns colourless as the coppery/reddy/brown Cu^{1+} ions are precipitated).

Other Reactions of Aldehydes

- The reduction of an Aldehyde to a 1˚ Alcohol by $LiAlH_4$ or $NaBH_4$.
- An Aldehyde will turn Brady's reagent (2,4-DNPH, $C_6H_3(NO_2)_2NHNH_2$) a yellowy/orange colour.

  Reaction Equation: $\mathbf{RR'}C=O + C_6H_3(NO_2)_2NHNH_2 \rightarrow C_6H_3(NO_2)_2NHN=C\mathbf{RR'} + H_2O$

  where the 2,4-DiNitroPhenylHydraz**i**ne becomes 2,4-DiNitroPhenylHydraz**o**ne.
- Iodoform reaction: An Aldehyde will with Iodine and Sodium Hydroxide to form RCOOH and yellow CHI_3.
- An Aldehyde will react with HCN or acidified NaCN to form first a Nitrile and then an Amide and then an Acid.

• Primary (1˚), Secondary (2˚), and Tertiary (3˚) Alcohols can behave very differently from each other. In all three of the following Oxidisation reactions, Sulphuric plus and an excess of a Chromate (VI) ion[1] i.e. a Cr^{6+} ion (from say either Potassium or Sodium Dichromate) is used to provide the **Oxidising agent**. *Both the Chromium and the Potassium ions will become Sulphates during these reactions.*

• If you mix a 1˚ Alcohol with concentrated Sulphuric Acid[2] and an Oxidising agent such as Potassium Dichromate in a test tube, **then just the heat from your hand will cause the 1˚ Alcohol to be Oxidised into an Aldehyde**, *but if you subsequently heat the mixture then you will cause the **Aldehyde** to be further Oxidised into a **Carboxylic Acid**.*

[1] The orange Cr (VI) ion is the Oxidising agent, and you will need *AN EXCESS* of it – otherwise you will run out of the Oxidising agent before the reaction is completed! You can, if you so desire, distil off the Aldehyde as it is formed and this will prevent it from being further oxidised into a Carboxylic Acid.
[2] It will not work with dilute H_2SO_4.

- This is one of the classic tests for the oxidisation of an Alcohol into either an aldehyde or into an acid, so please learn it off by heart "Orange to Green, *ORANGE TO GREEN*, **ORANGE TO GREEN!** Please never forget that: **ORANGE** to **GREEN**"! The Chromate (VI) ion has an orange colour – but the Cr (VI) ion will be *reduced* to a blue Cr (III) ion during the reaction (as it loses Oxygen to the Alcohol) – therefore as the blue Cr (III) ion is formed it mixes with the orange Cr (VI) ion, and in Physics (and in Painting), blue plus orange gives you green.

- Could you now please calculate the Oxidisation Numbers of **Cr** in $K_2Cr_2O_7$, and in $Cr_2(SO_4)_3$. [The answers that you should have arrived at are "+6" for Cr in $K_2Cr_2O_7$ (and Cr^{6+} has an **orange** colour) and "+3" in $Cr_2(SO_4)_3$ (and Cr^{3+} has a **blue** colour[3]). *[I trust that you remember that you have to reverse the sign and the number when they are shown as an exponent integer i.e. the number "+3" becomes the oxidisation state Cr^{3+}!]*

NB In Organic Chemistry it is permitted to use an Oxygen atom inside square brackets, i.e. "[O]", to indicate that Oxygen is oxidising an organic substance. You will see this convention used on the next few pages. In modern Chemistry notation, we also tend NOT to show the electrons that are being lost by the Alcohol in the reaction. For example we no longer write

R–CH₂OH – 2H⁺ – 2e⁻ —> R–CHO **[an Oxidisation Reaction]**
Alcohol — Aldehyde

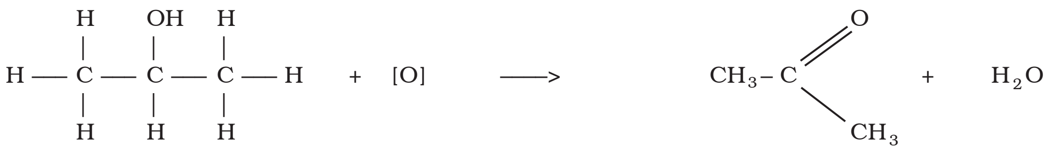
$$\underset{\text{Alcohol}}{R\text{–}CH_2OH} - 2H^+ - 2e^- \longrightarrow \underset{\text{Aldehyde}}{R\text{–}CHO} \quad \textbf{[an Oxidisation Reaction]}$$

<u>The Oxidisation of Secondary Alcohols (2° Alcohols) into Ketones</u>

The Oxidisation of a 2° Alcohol $\xrightarrow[\text{"Heat" (or "Reflux")}]{\text{excess } Cr_2O_7^{2-} \text{ / conc } H_2SO_4}$ **A KETONE**

e.g.	Propan-2-ol			—>	Propanone		
	$CH_3CH(OH)CH_3$	+	[O]	—>	CH_3COCH_3	+	H_2O

NB You must have an excess of $Cr_2O_7^{2-}$ *otherwise you will run out of the Oxidising agent before the reaction is completed!*



NB You must have an excess of $Cr_2O_7^{2-}$ *otherwise you will run out of the Oxidising agent before the reaction is completed! You do not need to show the Water if you do not want to.* We will talk about converting a Ketone back into a 2°alcohol by refluxing it with either $NaBH_4$ or $NaAlH_4$ next year.

- The Oxidisation of Primary/Secondary/and Tertiary Alcohols are **frequently** tested in your exams, so let me repeat what I have told you!

- **<u>Reactions of/Tests for 1° vs. 2° vs. 3° Alcohols</u>**

  Under GENTLE Oxidisation, (I will repeat that, under GENTLE Oxidisation)

  1° Alcohols –> <u>ALDEHYDES</u>, and then <u>ALDEHYDES</u> –> <u>CARBOXYLIC ACIDS</u>.
  2° Alcohols –> <u>KETONES</u>.
  3° Alcohols : resist gentle oxidisation.

[3] Some people say it is blue, others say it is green. **Please do not get hung up on the colour (but it is BLUE).** The blue and the orange together make it look **GREEN**!