

A Second Year Blog on Aldehydes (R-CHO) (for the week commencing the 22nd of December 2019)

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 oxidation therefore there is no colour change. However, with Primary and Secondary Alcohols the oxidation to an Aldehyde or to a Ketone (respectively) is accompanied by a colour change **from orange to green**.

The oxidation 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 AgNO₃ 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 Cu²⁺ ions in the solution are converted into Cu¹⁺ ions and the solution turns colourless as the coppery/reddy/brown Cu¹⁺ ions are precipitated).

Other Reactions of Aldehydes

- The reduction of an Aldehyde to a 1° Alcohol by LiAlH₄ or NaBH₄.
- An Aldehyde will turn Brady's reagent (2,4-DNPH, C₆H₃(NO₂)₂NHNH₂) a yellowy/orange colour.
Reaction Equation: **RR'C=O** + C₆H₃(NO₂)₂NHNH₂ → C₆H₃(NO₂)₂NHN=C**RR'** + H₂O
where the 2,4-DiNitroPhenylHydrazine becomes 2,4-DiNitroPhenylHydrazone.
- Iodoform reaction: An Aldehyde will with Iodine and Sodium Hydroxide to form RCOOH and yellow CHI₃.
- 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) ion¹ i.e. a Cr⁶⁺ 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 Acid² 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 H₂SO₄.

- This is one of the classic tests for the oxidation 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 Oxidation 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 colour³). [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 oxidation 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

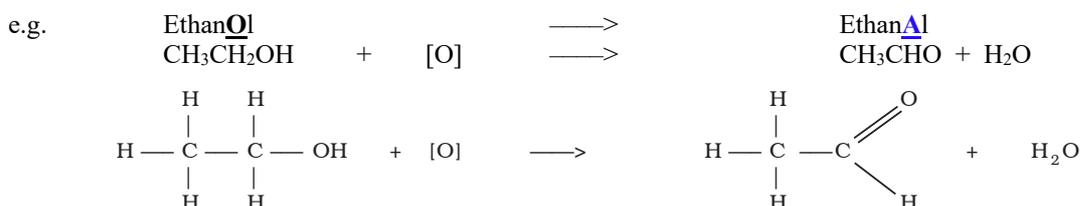


The Oxidation of Primary Alcohols (1° Alcohols) into first Aldehydes and then into Acids

(The mechanisms of these reactions is not shown and is not required at ‘A’ Level.)

Step 1

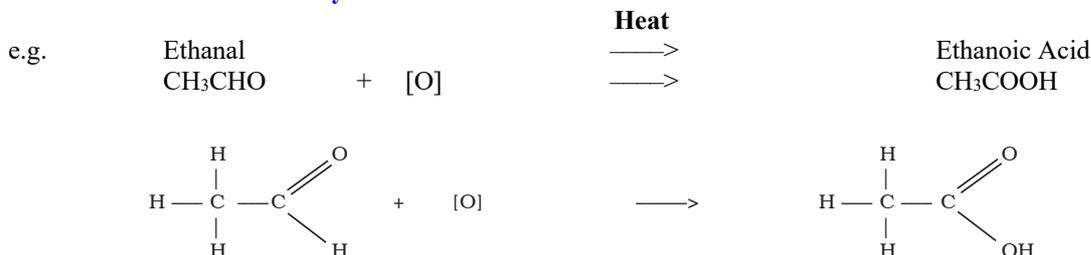
The Oxidation of a 1° Alcohol $\xrightarrow[\text{ROOM TEMP}]{\text{excess } Cr_2O_7^{2-} / \text{conc } H_2SO_4}$ An ALDEHYDE



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 do so. You can distil off the Aldehyde as it is formed if you do not want the Aldehyde to be converted into a Carboxylic Acid at this stage.

Step 2

The Oxidation of an Aldehyde $\xrightarrow[\text{Heat}]{\text{excess } Cr_2O_7^{2-} / \text{conc } H_2SO_4}$ A CARBOXYLIC ACID



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!

The overall reaction from an Alcohol to an Acid is thus $CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$.

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!

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

- Reactions of/Tests for 1° vs. 2° vs. 3° Alcohols

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

1° Alcohols → ALDEHYDES, and then ALDEHYDES → CARBOXYLIC ACIDS.

2° Alcohols → KETONES.

3° Alcohols : resist gentle oxidation.