Carboxylic acids and derivatives (A Level)

Benzoic acid, acyl chloride formation, oxidation of methanoic and ethanedioic acids, relative acidities, esters from acyl chlorides, and the addition–elimination reactions of acyl chlorides.

33.1 Carboxylic acids

Benzoic acid

Made by heating an alkylbenzene, for example **methylbenzene**, with **hot alkaline** $KMnO_4$, then adding dilute acid to give the free acid: $C_6H_5CH_3 \rightarrow C_6H_5COOH$.

Forming acyl chlorides

Carboxylic acids react with PCl_5 (room temperature), PCl_3 (heat) or $SOCl_2$ (thionyl chloride, heat) to give an **acyl chloride**:

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

$SOCl_2$ is convenient because its by-products, SO_2 and HCl, are gases.

Carboxylic acids that can be oxidised further

- **Methanoic acid**, $HCOOH$, has an aldehyde-like H, so it is oxidised by **Fehling's** or **Tollens' reagent**, acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ to **carbon dioxide and water**.
- **Ethanedioic acid**, $HOOC{-}COOH$, is oxidised by warm acidified $KMnO_4$ to **carbon dioxide**: $5HOOCCOOH + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$.

Relative acidities

Carboxylic acids are weak acids, **stronger than phenol, which is stronger than water and alcohols**. In the carboxylate ion $RCOO^-$ the charge is **delocalised over two oxygen atoms** (both C–O bonds equal in length), which stabilises it more than the phenoxide ion, where the charge is delocalised into the ring (less effectively), or the alkoxide ion (no delocalisation).

Substituents: electron-withdrawing groups, such as chlorine, **increase acidity** by spreading the negative charge on the carboxylate ion (the negative inductive effect) and stabilising it. The more chlorine atoms, and the nearer to the –COOH, the stronger the acid:

$$CH_3COOH\ (pK_a\ 4.76) < CH_2ClCOOH\ (2.87) < CHCl_2COOH\ (1.35) < CCl_3COOH\ (0.66)$$

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Electron-donating alkyl groups **decrease** acidity: ethanoic acid is weaker than methanoic acid.

Explain acidity using the species after proton loss

The carboxylate ion has two equivalent C–O bonds and negative charge distributed over both oxygens. Electron-withdrawing substituents stabilise this ion further through inductive effects; electron donation tends to oppose that stabilisation. An acidity argument should compare conjugate-base stability, not claim that chlorine physically attracts and pulls a proton out of solution.

Worked comparison: 2-chlorobutanoic acid has chlorine closer to COOH than 4-chlorobutanoic acid. Its withdrawing effect is stronger at the acid group, so it is generally more acidic. Adding further nearby chlorines reinforces the effect. Lower pK_a corresponds to higher K_a and stronger acidity, reversing the numerical ranking if one simply sorts the pK_a values from smallest to largest.

> **TRY IT**
>
> Why can two acids of equal concentration have different pH even though both contain one COOH group?

Answer: Their ionisation equilibrium constants differ because the substituents change conjugate-base stability. Equal initial moles do not imply equal equilibrium hydrogen ion concentrations.

Oxidation exceptions and carbon accounting

Ordinary alkanoic acids resist further mild oxidation, but methanoic and ethanedioic acids are important exceptions. Methanoic acid can form CO_2 and water. Ethanedioic acid loses both carbons as carbon dioxide during oxidation, and the manganate(VII) reaction is used in redox chemistry.

Worked calculation: from the supplied ethanedioic-acid equation, five moles acid react with two moles MnO_4^-. A 20.0 cm^3 titre of 0.0200 mol dm^{-3} manganate(VII) contains 0.000400 mol, corresponding to $0.000400(5/2) = 0.00100$ mol acid. That acid produces 0.00200 mol CO_2. State the 5 : 2 ratio rather than assuming acid and oxidant are 1 : 1.

33.2 Esters

Acyl chlorides react with alcohols and phenols at room temperature to give esters; this works for phenol, where direct esterification with a carboxylic acid does not:

$$CH_3COCl + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HCl \qquad C_6H_5COCl + C_6H_5OH \rightarrow C_6H_5COOC_6H_5 + HCl$$

The second gives phenyl benzoate. (Phenol is first dissolved in NaOH to make the more reactive phenoxide ion.)

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Building an ester from the activated acid derivative

Acyl chlorides can acylate alcohols and suitable phenolic reagents. The carbonyl-containing fragment remains on the acid side, while the attacking oxygen supplies the ester O–R connection. Unlike reversible direct esterification, the chloride route has a reactive leaving group and produces HCl rather than water as its principal small by-product.

Worked example: benzoyl chloride plus ethanol gives ethyl benzoate, not phenyl ethanoate. Ethanoyl chloride plus phenol gives phenyl ethanoate. Reversing which fragment contains the ring changes connectivity even if the final product names both contain "phenyl" and "ethan-". Draw the ester bonds before naming it.

Phenoxide is more nucleophilic than neutral phenol, so alkaline phenol can facilitate acylation. However, water/hydroxide can also hydrolyse acyl chloride. The stated preparative method balances these competing reactions; "excess water is always helpful" is not valid for every ester synthesis.

> TRY IT
>
> Give the structure formed from propanoyl chloride and methanol.

Answer: Methyl propanoate, $CH_3CH_2COOCH_3$, with HCl. The carbonyl carbon is included in the propanoyl fragment's three-carbon count.

33.3 Acyl chlorides

Preparation: from a carboxylic acid with PCl_5, PCl_3 or $SOCl_2$ (see above).

Reactions (all at room temperature)

Reagent	Product
Water	carboxylic acid and HCl (steamy white fumes)
Alcohol	ester and HCl
Phenol	ester and HCl
Ammonia	**amide** and HCl (forms NH_4Cl with excess ammonia)
Primary or secondary amine	**N-substituted amide** and HCl

$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$. $CH_3COCl + C_2H_5NH_2 \rightarrow CH_3CONHC_2H_5 + HCl$.

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Mechanism: nucleophilic addition–elimination

The carbonyl carbon is attached to two electronegative atoms (O and Cl), so it is strongly $\delta+$.

1. **Addition:** the lone pair on the nucleophile (H_2O, ROH, NH_3) attacks the C of C=O, and the C=O π bond breaks onto oxygen, forming a tetrahedral intermediate with O^-.
2. **Elimination:** the lone pair on oxygen reforms the C=O, and **Cl^- leaves**; loss of H^+ from the attacking atom gives the product and HCl.

Relative ease of hydrolysis

Compound	Reaction with water	Reason
Acyl chloride, CH_3COCl	**violent, cold**	carbon is attached to O and Cl, so strongly $\delta+$; C–Cl breaks easily; an open path for attack
Alkyl chloride, CH_3CH_2Cl	very slow, needs heat with NaOH	only one electronegative atom; $\delta+$ carbon is much less $\delta+$
Aryl chloride, C_6H_5Cl	**no reaction**	C–Cl strengthened by overlap of the Cl lone pair with the ring

So the order of ease of hydrolysis is **acyl chloride > alkyl chloride > aryl chloride**.

Follow charge through addition–elimination

Begin with the nucleophile's lone pair attacking carbonyl carbon, while the pi pair moves onto oxygen. Carbon now has four single bonds in a tetrahedral intermediate. The incoming neutral nucleophile may carry a positive charge after making an extra bond, while the former carbonyl oxygen is negative. Omitting these charges can produce an intermediate with impossible electron accounting.

Next the oxygen lone pair reforms C=O and the C–Cl bond pair moves to chloride. Proton transfer gives the neutral ester, acid or amide. Depending on the representation, deprotonation can be shown before or after collapse, provided each step is chemically consistent and overall atoms/charge balance. Do not draw chloride leaving while leaving carbon with five completed bonds.

Worked ammonia equation: $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$. One ammonia supplies the amide nitrogen and another traps the acidic proton/HCl. With a primary amine, excess amine similarly can form an alkylammonium chloride as well as the N-substituted amide. A simplified one-amine equation showing HCl is an overall accounting form, not necessarily the final speciation in excess amine.

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What product results from ethanoyl chloride and methylamine, and where does the methyl group appear?

Answer: N-methylethanamide, $CH_3CONHCH_3$. One methyl belongs to the ethanoyl fragment and one remains attached to nitrogen from the amine. The product is an amide, not a tertiary amine.

Compare three different C–Cl environments

An acyl chloride has an electrophilic carbonyl carbon and a leaving chloride, enabling the addition–elimination route. An alkyl chloride lacks the carbonyl but can undergo SN1/SN2 according to structure and conditions. An aryl chloride has strengthened C–Cl bonding and lacks the ordinary alkyl substitution pathways. The comparison is not explained solely by counting electronegative neighbours; the available mechanism and bond character also matter.

Worked interpretation: cold water can hydrolyse ethanoyl chloride rapidly and acidify the mixture through acid/HCl formation. Chloroethane reacts much more slowly under analogous mild conditions. Chlorobenzene resists the routine hydrolysis. A silver-nitrate result must therefore be interpreted after considering whether free chloride has actually been released.

Work-up and practical observations

Anhydrous acyl chlorides can fume in moist air because water reacts to produce HCl-containing droplets. In an aqueous product mixture, hydrogen chloride dissolves and supplies hydrogen and chloride ions. Use “steamy fumes” for the appropriate physical setting rather than claiming a white precipitate is necessarily the product of every hydrolysis.

TRY IT

Why are dry conditions useful when an acyl chloride is intended to react with an alcohol rather than water?

Answer: Water competes as a nucleophile and converts acyl chloride into carboxylic acid. Preventing unwanted hydrolysis improves the amount available for ester formation.

Chapter check: explain acidity through conjugate-base effects, balance the exceptional oxidation reactions, track both ester fragments and preserve correct charges in tetrahedral intermediates.

Note Academy

References and further reading

Scope follows section 33 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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