19 Carboxylic acids and derivatives

This topic introduces the chemistry of carboxylic acids and their derivatives

19.1 Carboxylic acids ☐

19.2 Acyl chlorides ☐

ACYL CHLORIDES & ACIDS

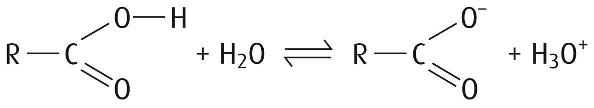
19 Carboxylic acids and derivatives

This topic introduces the chemistry of carboxylic acids and their derivatives.

	Learning outcomes Candidates should be able to:
19.1 Carboxylic acids	a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles b) describe the reactions of carboxylic acids in the formation of: (i) salts, by the use of reactive metals, alkalis or carbonates (ii) alkyl esters (iii) alcohols, by use of $LiAlH_4$ **(iv) acyl chlorides** **c) recognise that some carboxylic acids can be further oxidised:** **(i) the oxidation of methanoic acid, HCO_2H, with Fehling's and Tollens' reagents** **(ii) the oxidation of ethanedioic acid, HO_2CCO_2H, with warm acidified manganate(VII)** **d) explain the relative acidities of carboxylic acids, phenols and alcohols** **e) use the concept of electronegativity to explain the acidities of chlorine-substituted ethanoic acids**
19.2 Acyl chlorides	**a) describe the hydrolysis of acyl chlorides** **b) describe the reactions of acyl chlorides with alcohols, phenols, ammonia and primary amines** **c) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides including the condensation (addition-elimination) mechanism for the hydrolysis of acyl chlorides**

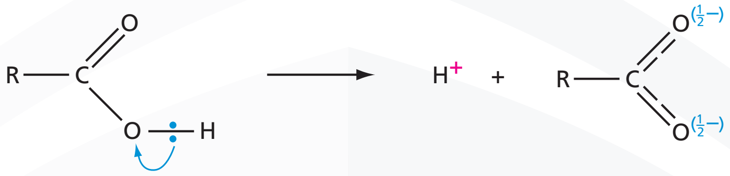
ACIDITY

Carboxylic acids are weak acids that dissociate partially in aqueous solution according to the equation:



carboxylate ion

They are more acidic than alcohols because the negative charge on the anion can be delocalised over two electronegative oxygen atoms.



ACIDITY

The increasing acidities of alcohols, phenols and carboxylic acids are explained by the increasing ability of the molecular structures to delocalise the negative charge in the alkoxide, phenoxide and carboxylate anions.

Their relative acidities are demonstrated by their different reactions with sodium, sodium hydroxide and sodium carbonate.

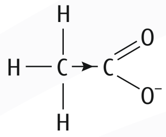
Reagent	**Observation with**		
	Hexanol	**Phenol**	**Hexanoic acid**
Na(s)	H_2(g) evolved	H_2(g) evolved	H_2(g) evolved
NaOH(aq)	no reaction	dissolves	dissolves
Na_2CO_3(aq)	no reaction	no reaction	CO_2(g) evolved

RELATIVE ACIDITIES

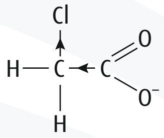
Atoms or groups that draw electrons away from the —CO_2^- group will help the anion to form, and this causes the acid to be more dissociated (that is, to become a stronger acid), e.g. halogens.

On the other hand, groups that donate electrons to the —CO_2^- group will cause the acid to become weaker, e.g. alkyl groups.

Electron-donating groups decrease the acid strength of carboxylic acids, whereas electron- withdrawing groups increase their acid strength.

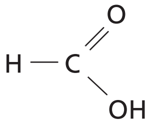
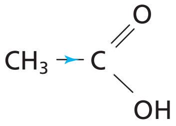
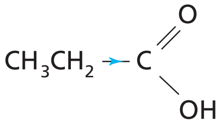


electron density donated to COO^- group

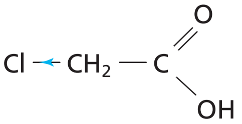
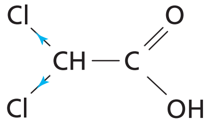
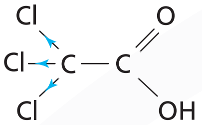


electron density withdrawn from COO^- group

RELATIVE ACIDITIES

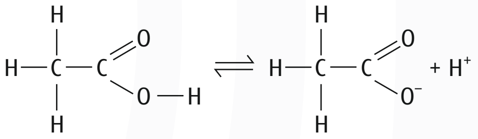
Formula of acid	pK_a	Percentage dissociation in 1.0 mol dm^{-3} aqueous solution
 $HCOOH$	3.75	1.3%
 CH_3COOH	4.76	0.42%
 CH_3CH_2COOH	4.87	0.36%

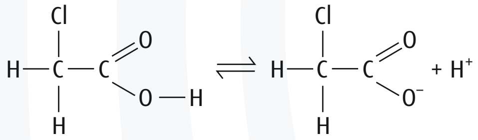
RELATIVE ACIDITIES

Formula of acid	pK_a	Percentage dissociation in 1.0 mol dm^{-3} aqueous solution
	2.87	3.7%
	1.26	21%
	0.66	59%

CHLOROETHANOIC ACID VS ETHANOIC ACID

Chloroethanoic acid is a stronger acid than ethanoic acid.


ethanoic acid ⇌ ethanoate ion


chloroethanoic acid ⇌ chloroethanoate ion

The difference in acidity can be explained by considering the stability of the anion (conjugate base) formed.

The more stable the anion (conjugate base) is, more likely is its formation.

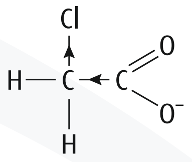
CHLOROETHANOIC ACID VS ETHANOIC ACID

The Cl is a very electronegative atom and, in the chloroethanoate ion, pulls electron density away from the CO_2^- group.

Since the COO group is less negative, it attracts the H^+ ion back less strongly.

The conjugate base is, therefore, more stable.

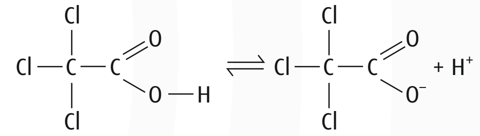
A more stable conjugate base indicates a greater tendency to dissociate and, therefore a stronger acid.



electron density withdrawn from COO^- group

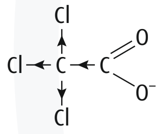
TRICHLOROETHANOIC ACID VS CHLOROETHANOIC ACID

Trichloroethanoic acid is a stronger acid than chloroethanoic acid.



trichloroethanoic acid

trichloroethanoate ion

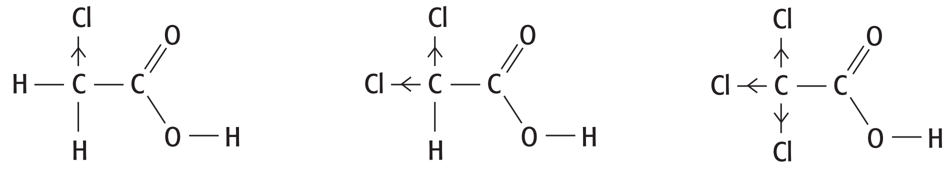


more electron density withdrawn from COO^- group

Three very electronegative Cl atoms have a greater electron-withdrawing effect than just one. More electron density is thus pulled away from the COO^- group making it less negative and less likely to attract back the H^+.

The trichloroethanoate ion is thus relatively more stable than the chloroethanoate ion and so trichloroethanoic acid dissociates more.

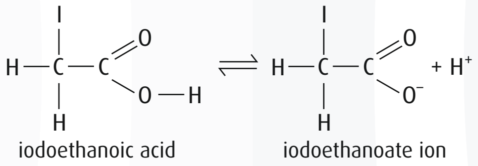
MULTIPLE CHLORINE SUBSTITUTES ON ACIDS



	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH
pK_a	2.87	1.29	0.65

CHLOROETHANOIC ACID VS IODOETHANOIC ACID

Chloroethanoic acid is a stronger acid than iodoethanoic acid.

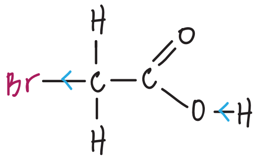


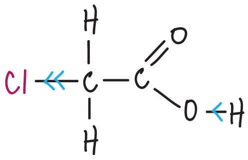
Iodine is a less electronegative atom than chlorine and thus withdraws less electron density from the CO_2^- group.

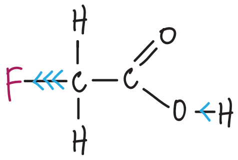
The COO group is thus more negative in the iodoethanoate ion and the H^+ ion is attracted back more strongly. The conjugate base is less stable and the acid is weaker.

Iodoethanoic acid is, however, still a stronger acid than ethanoic acid because of the electron-withdrawing nature of the I atom.

HALOGENOCARBOXYLIC ACIDS



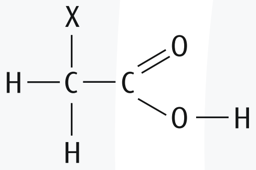




	$CH_2BrCOOH$	$CH_2ClCOOH$	CH_2FCOOH
pK_a	2.9	2.86	2.66

EFFECT OF SUBSTITUENTS ON ACIDITY

In general, for compounds of the form:

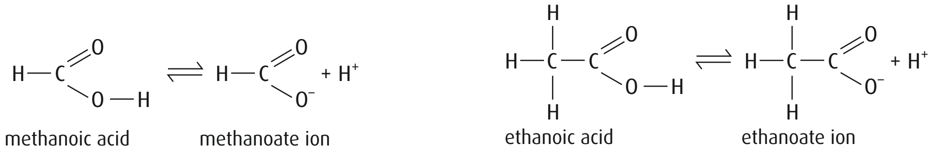


if X is an electron-withdrawing group, the acid will be a stronger acid than ethanoic acid due to stabilisation of the anion/conjugate base formed when the acid dissociates.

If X is an electron-releasing group the acid will be a weaker acid than ethanoic acid due to the increase the electron density on the COO group in the anion and the H^+ ion will thus be attracted back more strongly. The conjugate base is therefore less stable and the acid weaker.

ETHANOIC ACID VS METHANOIC ACID

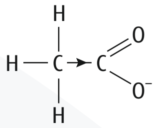
Ethanoic acid is a weaker acid than methanoic acid.



Ethanoic acid has an electron-releasing group attached to the CO_2^- group in the anion.

This increases the electron density on the COO group and therefore the H^+ is attracted back more strongly.

This means that the conjugate base is less stable for ethanoic acid and, it is, therefore a weaker acid.



electron density donated to COO^- group

LARGER CARBOXYLIC ACIDS

Beyond an ethyl group, the size of the alkyl group makes little difference to the electron-releasing effect.

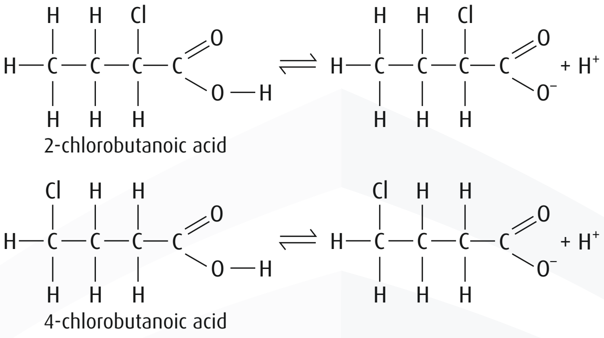
Thus propanoic acid is slightly stronger than ethanoic acid (the electron-releasing effect of an ethyl group is slightly greater than that of a methyl group) but propanoic acid, butanoic acid and pentanoic acid all have very similar acid strengths.

	$HCOOH$	CH_3COOH	C_2H_5COOH	C_6H_5COOH
pK_a	**3.77**	**4.76**	**4.88**	**4.2**

EFFECT OF DISTANCE OF Cl ATOMS ON ACIDITY

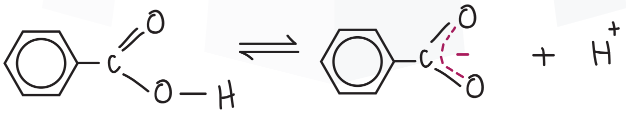
2-Chlorobutanoic acid is a stronger acid than 4-chlorobutanoic acid.

The further the Cl is from the CO_2^- group in the anion, the smaller the electron-withdrawing effect it has on it.

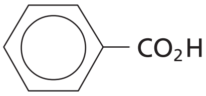
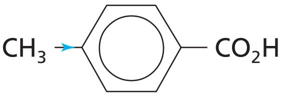
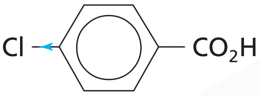


BENZOIC ACID

In benzoic acid, C_6H_5COOH, the pi orbital of the carbonyl group is in the same plane as the pi orbitals of the ring and hence the acid group is able to interact and attract electrons from the ring forming a more stable anion.



RELATIVE ACIDITIES

Formula of acid	pK_a	Percentage dissociation in 1.0 mol dm^{-3} aqueous solution
	4.20	0.80%
	4.37	0.73%
	3.99	1.0%

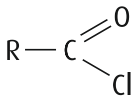
SKILL CHECK 1

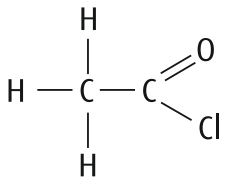
Arrange the following in order of acid strength (weakest first):

phenol, 2-chloropropanoic acid, ethanol, 3-chloropropanoic acid, propanoic acid, 2,2-dichloropropanoic acid, 2,2-difluoropropanoic acid, and 2-methylphenol.

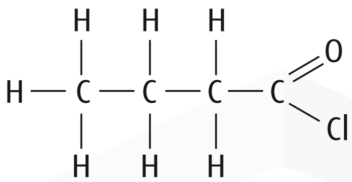
ACYL CHLORIDES

The basic structure of an acyl chloride is:

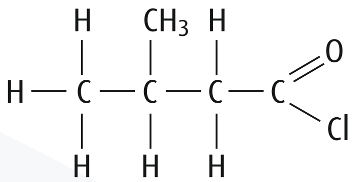




ethanoyl chloride



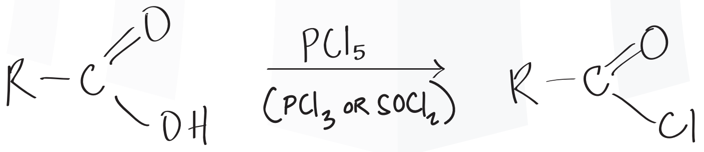
butanoyl chloride



3-methylbutanoyl chloride

FORMATION

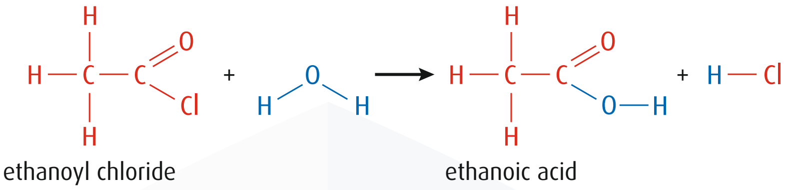
We can prepare acyl chlorides from their corresponding carboxylic acid using phosphorus(V) chloride, phosphorus(III) chloride or sulfur dichloride oxide ($SOCl_2$)

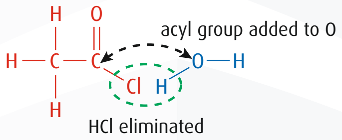


REACTIVITY

The electronegativity of the oxygen, and the easily polarised C=O double bond, have a dramatic effect on the reactivity of acyl chlorides compared with that of chloroalkanes.

Acyl chlorides react readily with water:



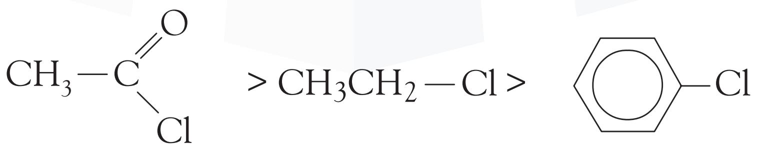


REACTIVITY

The electronegativity of the oxygen, and the easily polarised C=O double bond, have a dramatic effect on the reactivity of acyl chlorides compared with that of chloroalkanes.

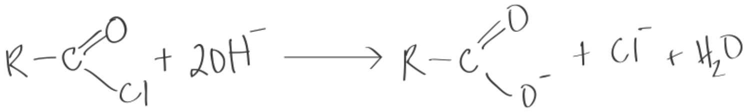
Acyl chlorides react readily with water unlike halogenalkanes and halogenobenzene.

The relative rates of hydrolysis are as follows:



HYDROLYSIS WITH ALKALI

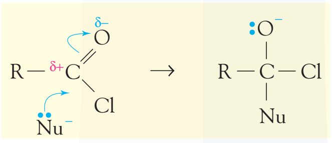
The hydrolysis of acyl chlorides is much faster with alkalis as OH⁻ is a stronger nucleophile than water.



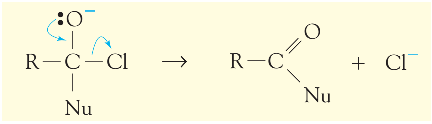
$$R-C(=O)Cl + 2OH^- \longrightarrow R-C(=O)O^- + Cl^- + H_2O$$

ADDITION ELIMINATION REACTION

The carbonyl group in acyl chlorides can undergo nucleophilic addition in a similar manner to carbonyl compounds:



Unlike carbonyl compounds, however, acyl chlorides are provided with an easily removed leaving group, the chloride ion:

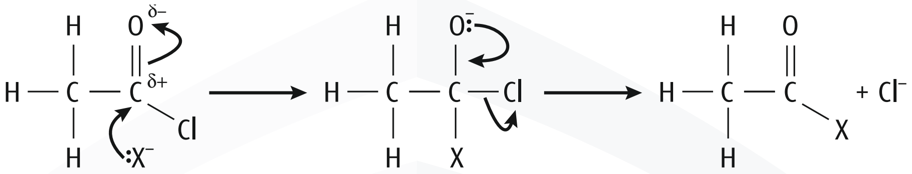


ADDITION ELIMINATION REACTION

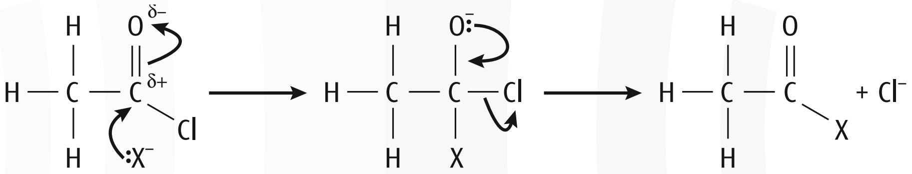
The mechanism of these reactions involves two steps:

1. initial addition of the nucleophile
2. elimination of the elements of HCl.

The basic mechanism can be illustrated by representing the nucleophile as X–:



ADDITION ELIMINATION REACTION



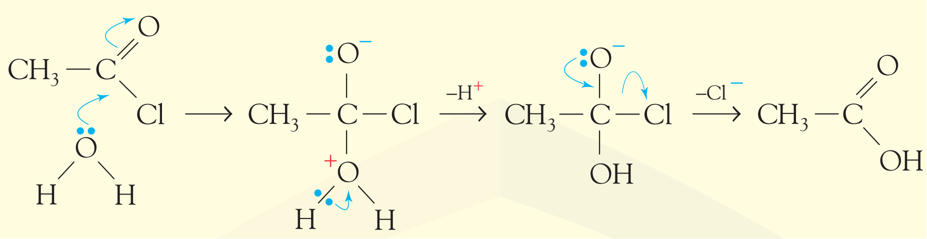
The nucleophile attacks the δ^+ C of the C=O group.

The π component of the C=O breaks with the pair of electrons going to the O to generate O–.

A lone pair from the O then is used to re-form the double bond and at the same time the C–Cl bond breaks.

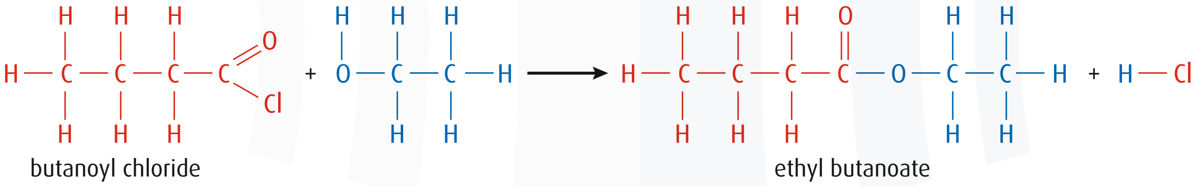
ADDITION ELIMINATION REACTION

Nucleophilic substitution has taken place, by a mechanism involving addition, followed by elimination. If the nucleophile is water, the carboxylic acid is formed:



REACTION WITH ALCOHOLS

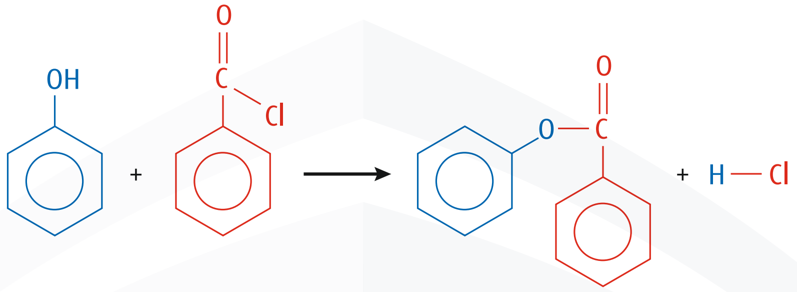
Acyl chlorides react with alcohols to form esters.



REACTION WITH ALCOHOLS

An alkaline solution of phenol reacts with benzoyl chloride to form phenyl benzoate.

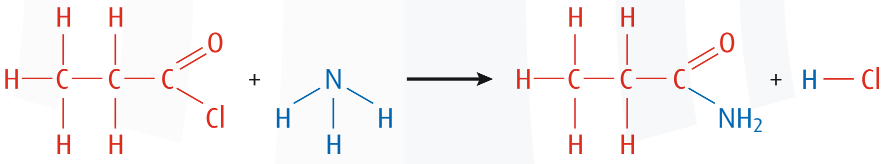
The phenol is dissolved in NaOH, to make phenoxide which is a stronger nucleophile, to make the yield better.



phenyl benzoate

REACTION WITH AMMONIA

When concentrated ammonia solution is added to an acyl chloride at 0°C a primary amide is formed.



propanamide

REACTION WITH AMINES

When acyl chlorides are reacted with amines (at low temperature) N-substituted amides are formed.