Chem Factsheet

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# Addition – Elimination Reactions

The number of organic compounds and organic reactions means it is important to learn and understand the different patterns observed when chemical species interact with each other. These reaction mechanisms help chemists to better predict and model new chemical processes, for example, in the design and development of new pharmaceuticals.

Students must be familiar with the three common attacking species to fully understand organic reactions:

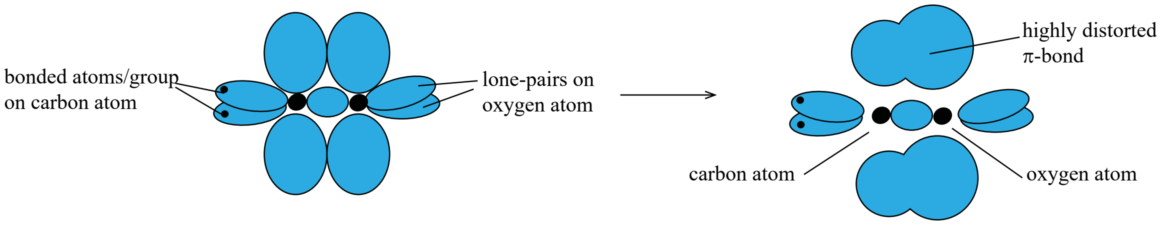
| Species | Description | Examples |
|---|---|---|
| Electrophiles | Electron-deficient chemical species that attack electron-rich sites, for example, double-bonds. They can accept a lone pair of electrons to form a bond. | $^{\delta+}Br–Br^{\delta-}$<br>H–Cl<br>$NO_2^+$ |
| Nucleophiles | Species able to donate a lone pair of electrons to an electron-deficient atom, for example, a carbocation, to form a bond. | $H_2O$:<br>$:NH_3$<br>$:OH^-$ |
| Radicals | An atom or molecule containing a single, unpaired electron. | Cl·or Br·<br>$·CH_3$ |

Addition-elimination reactions are also described as condensation reactions. These reactions occur when a nucleophile attacks and is added to a carbonyl carbon. A carbonyl group is a functional group consisting of a carbon atom double-bonded to an oxygen atom, C=O. This nucleophilic attack leads to the elimination of a leaving group. A leaving group is a small molecule, e.g. water, $H_2O$, hydrogen chloride, HCl, or ammonia, $NH_3$. The esterification of carboxylic acids with alcohols is an example of an addition-elimination reaction or condensation reaction. In this reaction the leaving group is a water molecule, $H_2O$.

$$CH_3COOH + C_2H_5OH \overset{H^+/Catalyst}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

Addition-elimination reactions occur due to the carbon-oxygen double bond in a carbonyl group. This double bond consists of a σ-bond (sigma), in the same plane as the bonding atoms' nuclei, and a π-bond (pi), which forms due to the side-on overlap of p-orbitals above and below the plane of the bonding nuclei, see Fig. 1.

**Fig. 1**

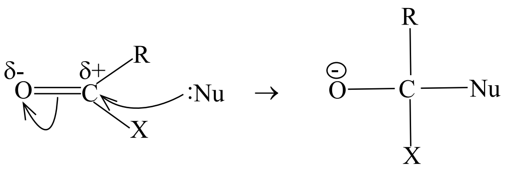


The distortion in the π-bond is due to the greater electronegativity of the oxygen atom compared to the carbon atom. This distortion determines the chemical behaviour of compounds containing carbon-oxygen double bonds. The following homogenous groups all contain a carbonyl group: aldehydes, ketones, carboxylic acids, acyl halides, acid anhydrides, amides, esters.

## Addition Reactions

Polarisation of the carbon-oxygen double bond occurs due the greater electronegativity of the oxygen atom. The carbonyl group is susceptible to nucleophilic attack via the electron-deficient carbonyl carbon atom. Nucleophiles are negative ions or polar molecules that are strongly attracted to a region of positive charge. They will contain a lone pair of electrons that is donated to the attacked species. Fig. 2 shows a nucleophile attacking the electron-deficient carbonyl carbon. The two electrons in the π-bond are pushed entirely onto the oxygen atom leaving the oxygen negatively charged.

**Fig. 2**



The nucleophilic attack of molecules containing a carbonyl group is described as a nucleophilic addition reaction.

The shape around the carbonyl carbon is trigonal planar, with bond angles around 120°. Attack of the carbonyl carbon will usually occur from above or below the plane. This may lead to the formation of optical isomers, or enantiomers, in a 50:50 racemic mix.

With reference to Fig. 2, when X is a hydrogen atom, X=H, or an alkyl group, X=R, then the outcome of nucleophilic attack on the carbonyl group is a nucleophilic addition reaction. This is because $H^-$ and $R^-$ are very poor leaving groups. The reduction of aldehydes and ketones to alcohols is an example of a nucleophilic addition reaction. Note the use of [H] to represent the reducing reagent, e.g. sodium tetrahydridoborate, $NaBH_4$, or lithium tetrahydridoaluminate, $LiAlH_4$ e.g.

Aldehyde $CH_3CH_2CHO + 2[H] \rightarrow CH_3CH_2CH_2OH$

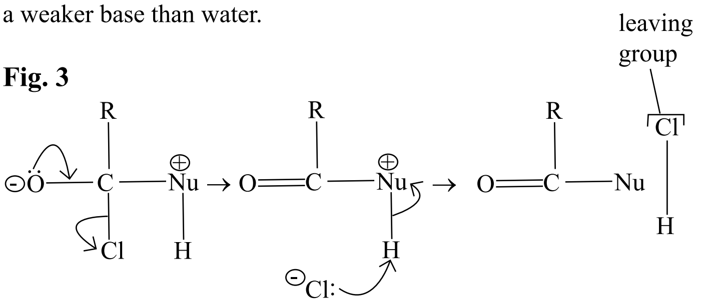
Ketone $CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$

## Elimination Reactions

Elimination reactions require the removal, or elimination, of adjacent atoms or groups of atoms resulting in the formation of multiple bonds. With reference to Fig. 2 above, when X is a highly electronegative atom bonded to the carbonyl carbon, there is potential for X to form part of a leaving group. These will include the following types of compounds: X=OH, carboxylic acids; X=Cl, acyl chlorides; $X=NH_2$, amides; $X=OR^1$, esters; or $X=OCOR^1$, acid anhydrides.

The success of this elimination step depends on the leaving group. Good leaving groups are weak bases, for example; water, $H_2O$, and alcohols, ROH. Generally, if X forms a better leaving group than water, then the carbonyl carbon-oxygen double bond will reform and $X^-$ will be eliminated. In the reaction described in Fig. 3, a hydrogen chloride molecule, HCl, forms as a leaving group. Hydrogen chloride is a better leaving group than a water molecule, because the chloride ion, $Cl^-$, is a weaker base than water.

**Fig. 3**



## Addition-Elimination Reactions

Addition-elimination reactions involve the attack by a nucleophile on a carbonyl carbon followed by the subsequent reformation of the carbonyl double bond and elimination of a good leaving group. The separate steps in the reaction are outlined in Fig. 4a and 4b. This describes a typical addition-elimination reaction, e.g. the acid catalysed esterification of ethanoic acid and ethanol. The mechanism is included to provide a better understanding of this reaction, but it is not required for A-level study.

Fig. 4a shows the protonation of the carbonyl oxygen by the acid catalyst. This leads to the formation of a carbocation that promotes a nucleophilic attack on the carbonyl carbon by the alcohol. The oxygen on the alcohol donates an electron-pair to the carbonyl carbon.

A carbocation is a molecule containing a three-bonded carbon atom and a positive charge. They are usually unstable and readily accept a lone pair of electrons.

**Fig. 4a**

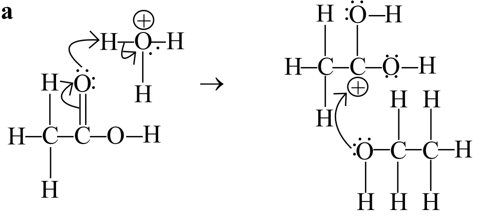
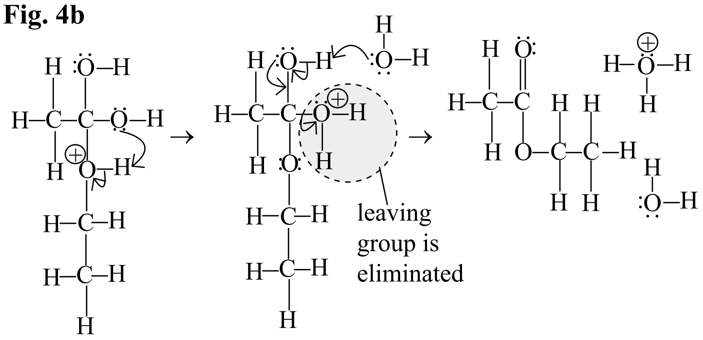


Fig. 4b describes the subsequent rearrangement about the carbonyl carbon, which leads to re-establishing the carbonyl carbon-oxygen double-bond and the elimination of water, $H_2O$. Note the regeneration of the acid-catalyst in the final step of the mechanism.

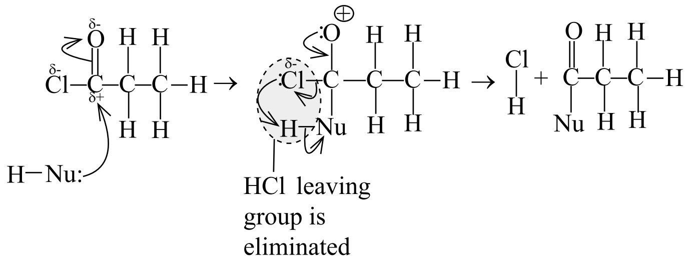
**Fig. 4b**



Acyl halides, for example acyl chlorides, ROCl, will undergo addition-elimination reactions. The attack by a nucleophile on the carbonyl-carbon atom is promoted by the action of highly electronegative chlorine atom drawing electron density from the carbonyl carbon. Although details of the reaction mechanism are not required by current A-level chemistry syllabuses, the reaction sequences are included to illustrate the reactions steps involved.

Fig. 5 describes the polarisation of the carbonyl carbon by adjacently bonded oxygen and chlorine atoms. The electron deficient carbonyl carbon atom is prone to attack by a nucleophile. An attacking nucleophile donates an electron-pair to form a new bond with the carbonyl carbon. This step involves the addition of the nucleophile to the carbonyl group. The π-bonded electrons on the carbon-oxygen carbonyl bond are pushed onto the oxygen atom. The subsequent rearrangement requires the elimination of a leaving group, which in this example is a hydrogen chloride molecule, HCl.

**Fig. 5**



Acid anhydrides react similarly to acyl chlorides with the elimination of a molecule of carboxylic acid. Using an alcohol as the nucleophile will result in the production of an ester.

Nitrogen containing nucleophiles with the general formula R-$NH_2$, undergo addition-elimination reactions with aldehydes and ketones. The nucleophilic addition step described in Fig. 6a leads to the formation of a hydroxyl group and a carbon-nucleophile single bond.

**Fig. 6a**

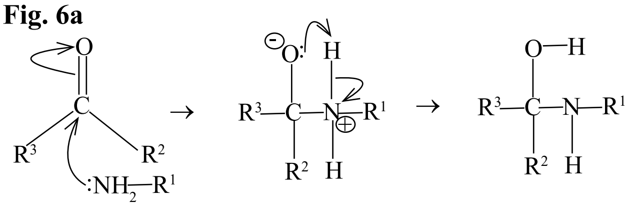
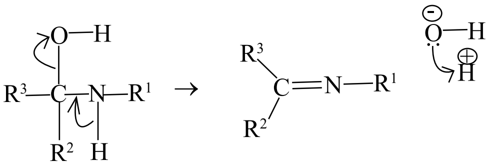


Fig. 6b describes the subsequent elimination of the leaving group. The elimination of water originates on the carbonyl oxygen and occurs because H–O bonds are stronger than H–N bonds.

**Fig. 6b**



The reaction of an amine with an acyl halide or acid anhydride will yield an amide or substituted amide, $R_1CONHR_2$ rather than the imine (C=N) formed in the reaction above.

## 2,4-Dinitrophenylhydrazine

2,4-dinitrophenylhydrazine is an important reagent used in chemistry. It is used to identify carbonyl compounds, i.e., aldehydes and ketones. A solution containing 2,4-dinitrophenylhydrazine and sulphuric acid is known as Brady's reagent. This simple chemical test involves adding drops of Brady's reagent to an aldehyde or ketone. A yellow-orange precipitate, the carbonyl derivative, is formed. This derivative is known as a 2,4-dinitrophenylhydrazone. For example, a reaction of ethanal will produce ethanal 2,4-dinitrophenylhydrazone. The identity of the initial aldehyde or ketone is determined by measuring the melting-point or boiling point of the derivative.

The reaction of the carbonyl and 2,4-dinitrophenylhydrazine undergoes addition-elimination. It is noted that knowledge of this mechanism as it applies to 2,4-dinitrophenylhydrazine is not required by current A-level syllabuses. The first step in the reaction describes the nucleophilic attack by 2,4-dinitrophenylhydrazine and the protonation step involving the oxygen on the carbonyl group, see Fig. 7a. This leads to the addition of the 2,4-dinitrophenylhydrazine nucleophile to the carbonyl functional group.

**Fig. 7a**

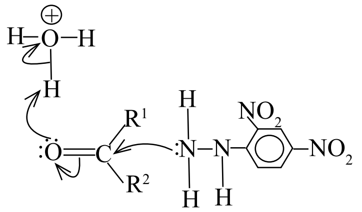


Fig. 7b describes further protonation steps, resulting in the removal of a hydrogen atom from the first nitrogen and oxygen accepting a proton on the hydroxyl group formed in the above step.

**Fig. 7b**

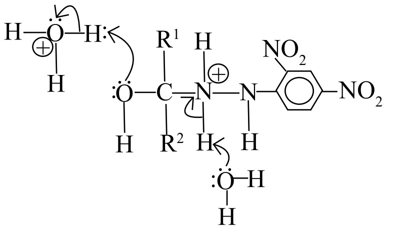
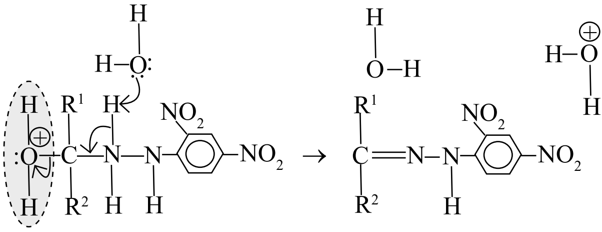


Fig. 7c shows the removal of a second hydrogen atom from the first nitrogen resulting in the formation of carbon-nitrogen double bond. Water forms the leaving group and is eliminated in the reaction.

**Fig. 7c**



$H_2O$ leaving group is eliminated

The derivative formed is the carbonyl 2,4-dinitrophenylhydrazone. This derivative is recrystallized, dried and its melting-point used to identify the original carbonyl compound.

## Addition-Elimination in Other Contexts

Addition-elimination reactions are common during the production of many biomolecules. The synthesis of proteins from amino acids as well as the production of starches from glucose can be classified as addition-elimination reactions.

Condensation polymerisation, for example in the manufacture of the polyester PETE or the polyamides nylon or Kevlar, is also a form of addition-elimination reaction.

## Questions

1. Complete chemical equations for each of the following reactions involving a carbonyl group. For each reaction, state whether the reaction described is a nucleophilic addition or addition-elimination reaction:
   (a) Propanone with hydrogen cyanide,
   (b) Ethanoyl chloride with phenol,
   (c) The reduction of ethanol by sodium tetrahydridoborate,
   (d) Ethanamide with sodium hydroxide (base conditions).
2. (a) Write a chemical equation describing the nucleophilic addition-elimination reactions between ethanoyl chloride, $CH_3COCl$, and water.
   (b) Ethanol chloride reacts violently with concentrated solution of ammonia producing a white solid mixture of ethanamide and ammonium chloride.
   Write the overall equation for the reaction.

## Answers

1. (a) $CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CH_3)CN$
   Nucleophilic addition reaction (No elimination/No leaving group).
   (b) $CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$
   Addition-elimination reaction. HCl leaving group.
   (c) $CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$
   Nucleophilic addition reaction (No elimination/No leaving group).
   Note that [H] is used to represent the reducing agent.
   (d) $CH_3CONH_2 + NaOH \rightarrow CH_3COONa + NH_3$
   Addition-elimination reaction. Ammonia, $NH_3$, leaving group.
2. (a) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$
   (b) $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$

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