

SECTION 16

RATES OF REACTION AND REACTION MECHANISM

Some reactions appear to occur instantaneously on mixing the reactants; that is to say too fast to follow by eye. Others are much slower and they can be followed over seconds, minutes or hours. The study of how fast reactions occur, i.e. the study of reaction rate, is known as kinetics, and the specific language and concepts which have been developed are introduced in this section. Studies of how the rate of a reaction depends on the concentrations of reactants, and sometimes products, have provided evidence for how an overall reaction proceeds, i.e. what we call the mechanism of a reaction. This section also introduces some basic classes of reaction mechanism which are widely used in describing and understanding chemical reactions.

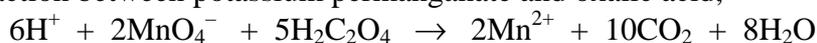
Chemical kinetics (kinetics): The study of the rates of chemical reactions and the steps by which they occur.

Rate: Rapidity of change, a property involving time.

Some chemical reactions are very fast and appear instantaneous to the eye on mixing the reactants, while others are very slow and the products only form over minutes, hours or even longer.

Reaction rate: The change in concentration of a reactant or product divided by the time it takes for the change to occur. Common units are $\text{mol L}^{-1} \text{s}^{-1}$.

[e.g. for the reaction between potassium permanganate and oxalic acid,



the decrease in concentration of permanganate over 40 s was found to be 0.12 mol L^{-1} . Thus the average change in concentration over this period was $\Delta[\text{MnO}_4^-]/t = -0.12 \text{ mol L}^{-1}/40 \text{ s}$ and the reaction rate could be expressed as the rate of loss of $\text{MnO}_4^- = 3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$. The rate of this reaction could also have been expressed as the rate of loss of $\text{H}_2\text{C}_2\text{O}_4$ ($7.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$) or as the rate of formation of CO_2 ($1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$).] In this example the numerical value of the rate depends on which reactant or product concentration is being measured. To overcome this it is possible to express the **rate of reaction** defined by its chemical equation.

Rate of reaction: Symbol, ν , for the reaction $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

the rate is equal to (rate of formation of C)/ c or (rate of formation of D)/ d or (rate of loss of A)/ a or (rate of loss of B)/ b [e.g. for the previous example $\nu = 1.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$].

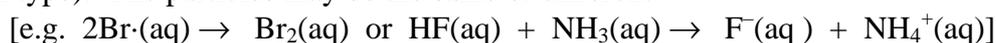
Most chemical reactions take place in a series of **elementary reactions (steps)**.

Elementary reaction: A one step reaction. There are three classes of elementary reaction.

Unimolecular reaction: An elementary reaction involving only one particle

[e.g. $\text{N}_2\text{O}_4(\text{aq}) \rightarrow 2\text{NO}_2(\text{aq})$].

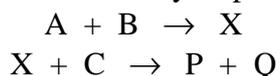
Bimolecular reaction: An elementary reaction involving only two particles (the most common type). The particles may be the same or different



Termolecular reaction: An elementary reaction involving only three particles. (Common in gas phase reactions where a third body is required to disperse the energy released from bond formation when two particles combine to give one [e.g. $2\text{Cl}\cdot(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}_2(\text{g})$ The molecule of chlorine initially present gains energy released by the formation of the new Cl-Cl bond].)

Molecularity: The number of particles (molecules, ions or radicals) taking part in an elementary reaction - 1 for unimolecular, 2 for bimolecular and 3 for termolecular.

Reaction mechanism: The sequential elementary steps of a reaction.



The overall reaction is $\text{A} + \text{B} + \text{C} \rightarrow \text{P} + \text{Q}$ and the species X is called a **reaction intermediate**.

Reaction intermediate: A species produced in one step of a chemical reaction but which is consumed in a later step. It is not a product of the overall reaction, and hence does not appear in the overall equation.

Rate-determining step: The slowest elementary step which effectively determines the overall rate of a reaction.

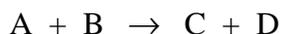
Rate equation (law): An equation relating the instantaneous rate of the reaction to the concentrations of reactants, products, or any other permanent species (such as **catalysts**) taking part in the reaction at that instance

[e.g. for the reaction $\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{H}_2\text{O}$ at pH of 7 the rate law is found by experiment to be: $v = k[\text{H}_2\text{O}_2][\text{I}^-]$

Rate coefficient (constant): Constant of proportionality in a rate law [e.g. k in the above rate law].

Reaction order: (a) With respect to a single species - the power to which the concentration of a single species is raised in a rate law [e.g. the above reaction is first-order in H_2O_2 and first-order in I^-]. (b) Overall - the sum of the powers of the species in the rate law [e.g. the above reaction is second-order overall. k is a second-order rate constant].

For a reaction between two species to occur they must collide, and most reactions take place in a series of bimolecular collisions, i.e by a series of bimolecular elementary steps. If the step involves two different species, A and B, the rate of collision, and therefore the rate of reaction, is proportional to the concentrations of A and B. Thus for the elementary bimolecular reaction



rate of reaction = $k[\text{A}][\text{B}]$ where k is called a **bimolecular rate constant**. A bimolecular rate constant is clearly 2nd order rate constant. For elementary reactions the order of the reactions are the same as the molecularity. As the units for rate of reaction are $\text{mol L}^{-1} \text{s}^{-1}$ it follows from the rate laws that the units of 1st order, 2nd order and 3rd order rate constants are respectively s^{-1} , $\text{L mol}^{-1} \text{s}^{-1}$ and $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$.

As bonds are often broken in elementary reactions not all collisions between reactant species lead to reaction, only those which collide with sufficient energy to overcome the **activation energy** barrier.

Activation energy: Symbol E_a . The minimum energy needed for colliding species to react, or cross the barrier. The magnitude of k depends on the height of the barrier, i.e. on the activation energy. The greater the E_a , the smaller the k , and the slower the reaction. The activation energy, E_a , is determined from an **Arrhenius plot**.

Arrhenius plot: A plot of $\ln k$ or $\ln \text{rate}$ against $1/T$ where T is the absolute temperature (temperature in kelvin). The slope of an Arrhenius plot equals $-E_a/R$ where R is the universal gas constant. This follows from the **Arrhenius equation**.

Arrhenius equation: $k = A \exp(-E_a/RT)$ ($k = Ae^{-E_a/RT}$) where A is called the Arrhenius pre-exponential factor.

The kinetic energy of molecules, and hence the fraction of collisions with energy in excess of E_a increases with increasing temperature. Therefore the rate of a reaction, and the magnitude of k , increase with temperature. The greater the E_a , the more sensitive the rate and rate constant to changes in temperature.

Unlike equilibrium constant expressions, the rate law for a reaction cannot be derived from inspection of the overall chemical equation but must be determined experimentally. Only for elementary reactions (i.e. one step reactions) can the rate law be deduced directly from the equation (as explained above).

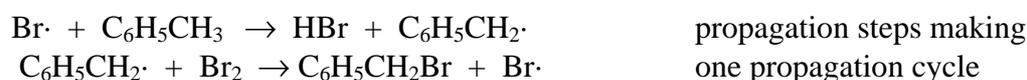
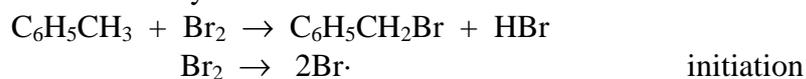
Information on reaction mechanisms can be obtained from experimentally obtained rate laws. While a rate law for a reaction can be derived for a postulated mechanism (because the rate law for each elementary step can be written), agreement between the experimental rate law and postulated mechanism does not prove the mechanism. Different mechanisms can lead to the same rate law.

Integrated rate equation: An equation which relates the concentration of a species at a given time to its initial concentration and the time, and which involves the rate constant [e.g. for the 1st order reaction $A \rightarrow \text{Products}$ $[A]_t = [A]_0 e^{-kt}$ where $[A]_t$ and $[A]_0$ are the concentrations of reactant A at time t and at the beginning of the reaction respectively].

Half-life: Symbol $t_{1/2}$, the time for the amount of a reactant in limiting amount (i.e. not in excess) to fall to half its original value. Commonly applied to radioactive isotopes [e.g. the half-life of cobalt-60, ^{60}Co , is 5.3 years].

Mean life-time: Symbol τ , the time for the amount of a reactant in limiting amount (i.e. not in excess) to fall to $0.368 (=1/e)$ of its original value. This is the average time a molecule must wait before undergoing reaction.

Chain reaction: A reaction in which an intermediate formed in an **initiation step** produces further reactive intermediates in the **propagation steps** until removed in a **termination step**. [e.g. For the photochemically initiated reaction between toluene and bromine



Chain length: The average number of propagating cycles between initiation and termination.

Catalyst: A substance which increases the rate of a reaction without being consumed in the overall reaction. It provides an alternative pathway or mechanism which increases the rate of the overall reaction. The catalyst is involved in the new pathway but if it is consumed in one step it is regenerated in a later step.

Homogeneous catalysis: The catalyst is in the same phase as the reactants [e.g. sulfuric acid in the esterification of an organic acid and alcohol].

Heterogeneous catalysis: The catalyst is in a different phase from the reactants. A solid catalyst adsorbs reacting species onto its surface where the reaction takes place [e.g solid V_2O_5 in the reaction of gaseous SO_2 and O_2 to form SO_3].

Classification and representation of reaction mechanisms

A detailed reaction mechanism uses structural formulae (Lewis or condensed as appropriate), and shows the details of the movement of electrons in bond breaking and bond making in each elementary step. For addition, substitution and some elimination reactions each step is considered a reaction between a substrate (the main reactant compound) and a reagent (a second reactant) which converts the substrate into a new species. The reagents are defined as **nucleophiles, electrophiles or free-radicals**.

Nucleophile: A chemical species seeking a nucleus with which to form a bond. To do this the species must have a pair of non-bonding electrons available to form a bond. A nucleophile is also a **Lewis base**.

Lewis base: An electron pair donor in a chemical reaction (see *page 14-6*).

Electrophile: A chemical species seeking a pair of electrons on a second species with which to form a bond. An electrophile is also a **Lewis acid**.

Lewis acid: An electron pair acceptor in a chemical reaction (see *page 14-6*).

Free-radical: A chemical species with an unpaired valence electron seeking an electron with which to form a bond. (see *page 1-4*)

Adduct: The product of an addition reaction.

Carbocation: A trivalent species with a positive charge, an electrophile and a Lewis acid [e.g. $(CH_3)_3C^+$, the positive carbon having only six valence electrons].

The mechanistic classification is combined with the structural classification and may include the reaction order (1st or 2nd) of the rate-determining elementary step and further information on the substrate. [e.g. $CH_3Cl + I^- \rightarrow CH_3I + Cl^-$ nucleophilic substitution second order, S_N2 , (nucleophilic attack of iodide ion on carbon replacing chlorine in one step, synchronous making and breaking of bonds)].

In representing details of bond breaking and making electron movement is shown using a "curly arrow",  for electrons moving as pairs, and  for electrons moving singly. The tail of the arrow is close to the electron(s) moving and the head shows where they are moving

to. Bond breaking and making is described as **heterolytic** or **homolytic**.

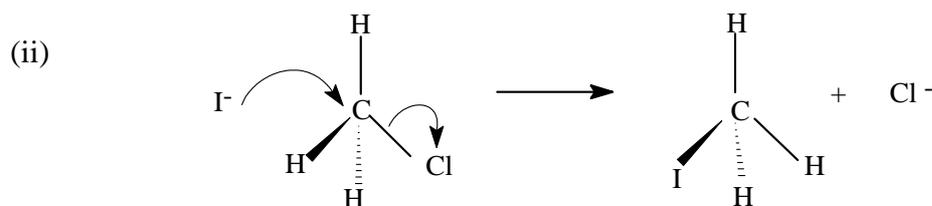
Heterolytic bond breaking or making: The pair of electrons of a bond move together
 [e.g. breaking $(\text{CH}_3)_3\text{C}-\text{Br} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$
 making and breaking $\text{I}^- + \text{CH}_3-\text{Cl} \rightarrow \text{I}-\text{CH}_3 + :\text{Cl}^-$].

Homolytic bond breaking: Electrons of a bond divide evenly to give two free-radicals
 [e.g. $\text{CH}_3\text{O}-\text{OC}_2\text{H}_5 \rightarrow \text{CH}_3\text{O}\cdot + \cdot\text{OC}_2\text{H}_5$].

Homolytic bond making: Pairing of an unpaired electron with a second electron from a bond of the substrate to form a new bond and a new radical; or dimerisation of two radicals to give a molecule [e.g. $\text{Cl}\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{Cl}-\text{CH}_2-\text{CH}_2\cdot$ or $\text{Br}\cdot + \cdot\text{Br} \rightarrow \text{Br}_2$]

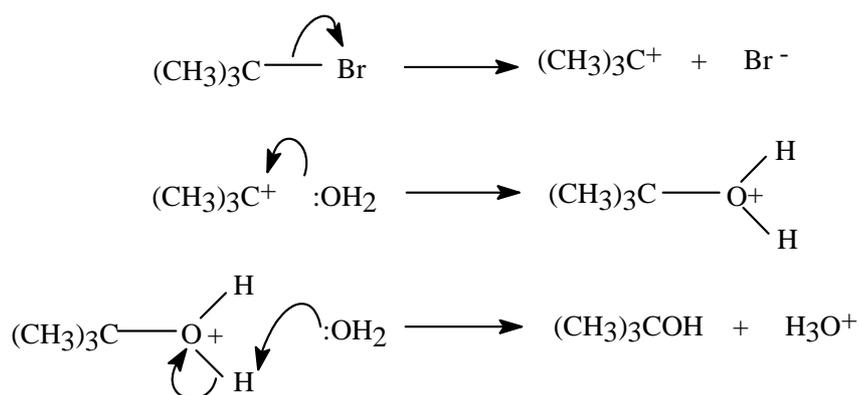
Full reaction schemes showing electron movement are given in the examples of mechanisms below. Note how it is not necessary to show non-bonding electron pairs. The tail of the curly arrow implies the presence of an electron pair.

(i) **Nucleophilic substitution second order, $\text{S}_{\text{N}}2$** [e.g. $\text{CH}_3\text{Cl} + \text{I}^- \rightarrow \text{CH}_3\text{I} + \text{Cl}^-$]
 (Nucleophilic attack of iodide ion on carbon replacing chlorine in one step, synchronous making and breaking of bonds.)

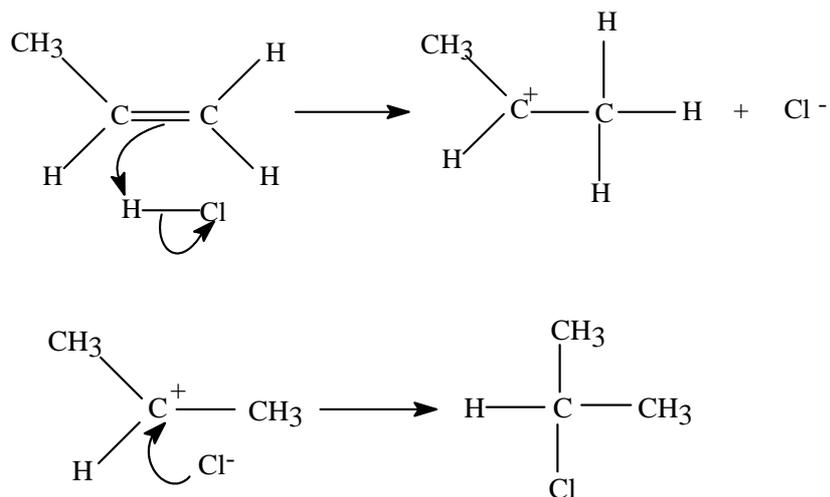
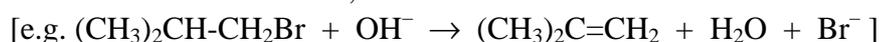


Nucleophilic substitution first order, $\text{S}_{\text{N}}1$

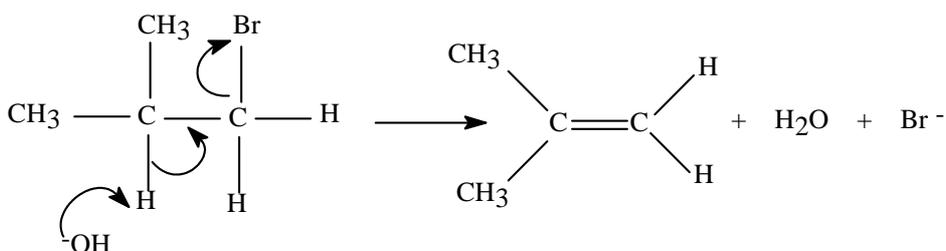
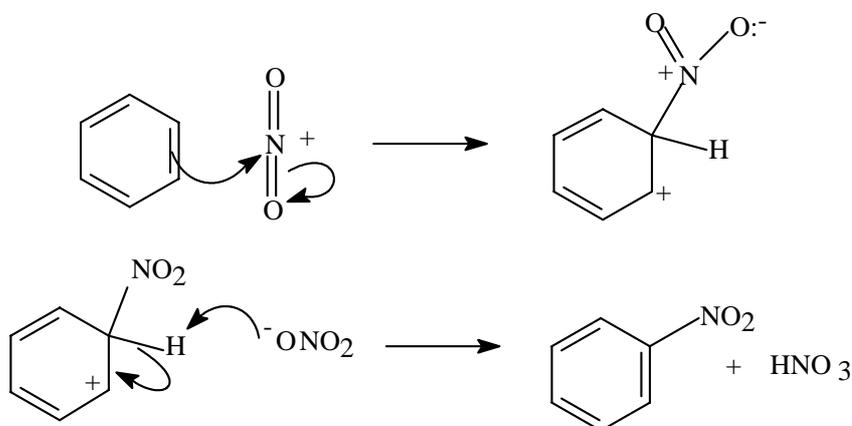
[e.g. $(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HBr}$] (The slow dissociation of the substrate to $(\text{CH}_3)_3\text{C}^+$ and Br^- followed by fast addition of water to the carbocation and loss of proton.)



(iii) **Electrophilic addition** [e.g. $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CHCl}-\text{CH}_3$]
 (Addition of a proton from HCl to the carbon utilising an electron pair of the double bond followed by fast addition of chloride to the carbocation intermediate.)

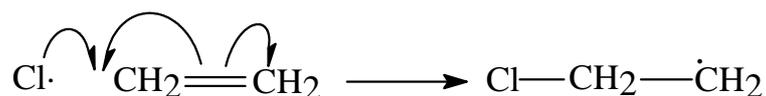
(iv) **Elimination second order, E2**

(Transfer of a proton from the secondary carbon atom to the hydroxide ion and loss of bromide ion in one step.)

(v) **Electrophilic aromatic substitution** [e.g. $\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$](The first and slow step involves the addition of NO_2^+ , an intermediate species from nitric acid, to a carbon atom of the benzene ring utilising a pair of electrons from the ring. This is followed by a fast proton transfer from the intermediate adduct.)

Note that the hydrogens are not shown on benzene itself, but when addition to a carbon atom occurs, the H atom on that carbon is shown.

(vi) **Free-radical addition** [e.g. $\text{Cl}\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2\text{Cl}-\dot{\text{C}}\text{H}_2$]



(vii) **Hydrogen abstraction** [e.g. $\text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}\cdot \rightarrow \text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2 + \text{HCl}$]

(This could be classified as attack of a chlorine atom on hydrogen replacing a benzyl group, i.e. a free-radical substitution reaction, but the simpler term hydrogen abstraction is always used for the removal of a hydrogen atom from a substrate by a free-radical.)



Note:

(1) that electron pairs and H atoms are not necessarily shown. They can be implied from the symbolism, or from the number of valence electrons in the structure shown.

(2) how important it is to do "electron book-keeping", and show formal charge.

This is the language used in research publications involving discussion of reaction mechanism - using the condensed structures consistent with the level of detail required.

EXERCISES

- Calculate the average rate of the following reactions in units of $\text{mol L}^{-1} \text{ s}^{-1}$ from the given concentration changes.
 - $\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$ when $[\text{Br}_2]$ changed from 0.34 to 0.25 mol L^{-1} in 90 seconds.
 - $6\text{H}^+ + 2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$ when $[\text{MnO}_4^-]$ changed from 0.40 to 0.27 mol L^{-1} in 48 minutes.
- The bimolecular reaction $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$ is one of the fastest known with a bimolecular rate constant of $1.0 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$. Calculate the rate of the reaction when equal volumes of 0.10 mol L^{-1} solutions of hydrochloric acid and sodium hydroxide are mixed. Remember that on mixing the two solutions the concentration of each reactant is changed.
- The reaction in question 1(a) is an electrophilic addition and occurs in two steps. In the first slow step a bromine atom becomes attached to C_1 and a bromide ion is formed. In the second step the bromide ion adds to the bromo-carbocation intermediate. Show the mechanism using curly arrows, and give the rate law.
- Give a structural and mechanistic classification of the reaction between toluene and bromine given as an example of a chain reaction on page 16-3.