Kinetics and Reaction Mechanisms (A2)

- Many reactions occur in a number of steps. This is call the reaction mechanism.
- These steps take place at its own rate and hence its own rate constant.
- The overall rate of a multi-step process depends on the slowest step.
- The slowest step is known as the rate determining step.
- investigation of the rate equation gives an idea of the steps involved in a reaction.
- A reactant that appears in the chemical equation may have no effect on reaction rate.
- A substance which is not a reactant in the chemical equation can affect reaction rate.

Example 1

- Reaction between Iodine and propane:

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

- The rate equation:

$$rate = k[CH_3COCH_3][H^+]$$

- $[H^+]$ in the rate equation because reaction is catalysed by acid
- $[I_2]$ not in the rate equation because the reaction has more than one step and the slowest step doesn't involve iodine.
- The rate determining step must therefore involve propanone and acid.

Verifying possible reaction mechanisms

- Kinetic data can only show that a proposed reaction mechanism is possible.
- The reaction mechanism is not deduced from the kinetic data.
- Example 1
  - Various mechanisms have been proposed for the rxn

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

  - one proposed mechanism:

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H^+ \overset{\text{fast}}{\rightleftharpoons} CH_3-\overset{+OH}{\overset{\|}{C}}-CH_3$$

$$CH_3-\overset{+OH}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{slow}} CH_3-\overset{OH}{\overset{|}{C}}=CH_2 + H^+$$

$$CH_3-\overset{OH}{\overset{|}{C}}=CH_2 + I_2 \xrightarrow{\text{fast}} CH_3-\overset{+OH}{\overset{\|}{C}}-CH_2I + I^-$$

$$CH_3-\overset{+OH}{\overset{\|}{C}}-CH_2I + I^- \overset{\text{fast}}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-CH_2I + HI$$

  - The rate equation for this reaction is

$$\text{rate} = k[CH_3COCH_3][H^+]$$

  - From the mechanism, the rate determining step (slow step) does not involve either propanone or hydrogen ions directly.
  - However, the intermediate $CH_3-\overset{+OH}{\overset{\|}{C}}-CH_3$ is derived from substances (propanone and hydrogen ions) which react together to form it. So both $[CH_3COCH_3]$ and $[H^+]$ appear in the rate equation.

- The reaction between iodine and the intermediate $CH_3C(OH)=CH_2$ is fast and iodine molecules are involved in the mechanism only after the rate-determining step.
- So the rate of reaction does not depend on the concentration of iodine.
- <u>Example 2</u>
- For the reaction:

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

- The rate equation is:

$$rate = k[N_2O_5]$$

- A suggested mechanism:

$$N_2O_5 \xrightarrow{slow} NO_2 + NO_3$$
$$NO_2 + NO_3 \xrightarrow{fast} NO + NO_2 + O_2$$
$$NO + NO_3 \xrightarrow{fast} 2NO_2$$

- Note that two molecules of N_2O_5 need to have reacted for subsequent steps to be completed.
- The rate equation tells us that the decomposition of individual molecules of nitrogen (V) oxide is the rate-determining step. This fits in with the proposed mechanism which suggest that the decomposition of N_2O_5 to form NO_2 and NO_3 is the slow step.
- The subsequent steps are very much faster by comparison, and do not influence the overall rate.

Exercise

An acidified solution of hydrogen peroxide reacts with iodide ions.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate equation for this reaction is:

$$rate = [H_2O_2][I^-]$$

The mechanism below has been proposed for this reaction.

$$H_2O_2 + I^- \xrightarrow{slow} H_2O + IO^-$$

$$H^+ + IO^- \xrightarrow{fast} HIO$$

$$HIO + H^+ + I^- \xrightarrow{fast} I_2 + H_2O$$

Explain why this mechanism is consistent with the rate equation.

Answers

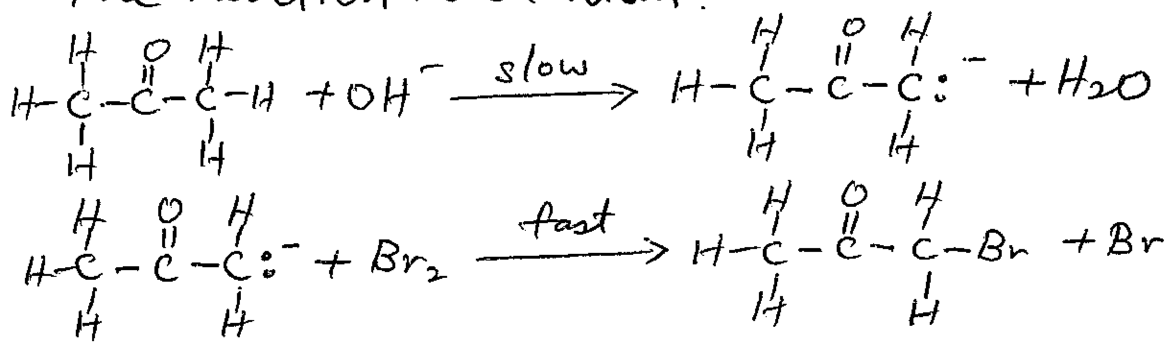
The rate equation shows that the rate determining step involved H_2O_2 and I^- ions. The hydrogen ions do not appear in the rate equation because they are involved in fast steps which takes place after the rate-determining step (slow step). So the proposed mechanism is consistent with the rate equation.

Predicting the order of a reaction from reaction mechanism

- If the intermediates present in the rate determining step (or substances which react together to form the intermediate) are identified, then we can predict the order of reaction from a given reaction mechanism.
- Example: the reaction of propanone with bromine in alkaline solution.

$$CH_3COCH_3 + Br_2 + OH^- \longrightarrow CH_3COCH_2Br + H_2O + Br^-$$

- The reaction mechanism.



- The slow step is the rate-determining step.
- The slow step involved one molecule of propanone and on hydroxide ion, so only these two species appear in the rate equation.
- The reaction is first order with respect to propanone and first order with respect to hydroxide ions.
- The overall order for the reaction is second order
- The rate equation, rate $= k[CH_3COCH_3][OH^-]$
- Bromine does not appear in the rate equation since it takes part in a fast step after rate determining step.

The hydrolysis of halogenoalkanes.

- Haloalkanes (RX) are hydrolysed by aqueous hydroxide ions:

  $RX + OH^-_{(aq)} \longrightarrow ROH + X^-$

- There are two possible mechanisms
- 1) if given rate equation:

  $$rate = k[RX][OH^-]$$

Mechanism 1 (hydrolysis of 1° and 2° haloakanes)

- one step reaction
- requires both species to collide
- rate is affected by both reactant
- second order overall.

Example

- $CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$
- $rate = k[CH_3CH_2-Br][OH^-]$

- The reaction is first order with respect to both the organic compound and the hydroxide ions.
- Both of these must be taking part in the slow step of the reaction.
- The reaction must happen by a straightforward collision between them.

$$\overset{\delta+}{CH_3-CH_2}-\overset{\delta-}{Br} \;\; (:\overset{-}{O}H) \longrightarrow CH_3-CH_2-OH \; + :Br^-$$

- The carbon atom which is hit by the hydroxide ion has a slight positive charge on it and the bromine atom a slight negative one because of the difference in their electronegativities.
- As the hydroxide ion approaches, the bromine is pushed off in one smooth action.

<u>Mechanism 2</u> (hydrolysis of 3° haloalkanes)

- two steps reactions : (i) $RX \longrightarrow R^+ + X^-$
  (ii) $R^+ + OH^- \longrightarrow ROH$
- Step (i) is slower as it involves bonds breaking and thus will be the rate determining step.
- rate depends only on [RX]

- 2) if given rate equation:

$$rate = k[RX]$$

<u>Mechanism 2</u> (hydrolysis of 3° haloalkanes)

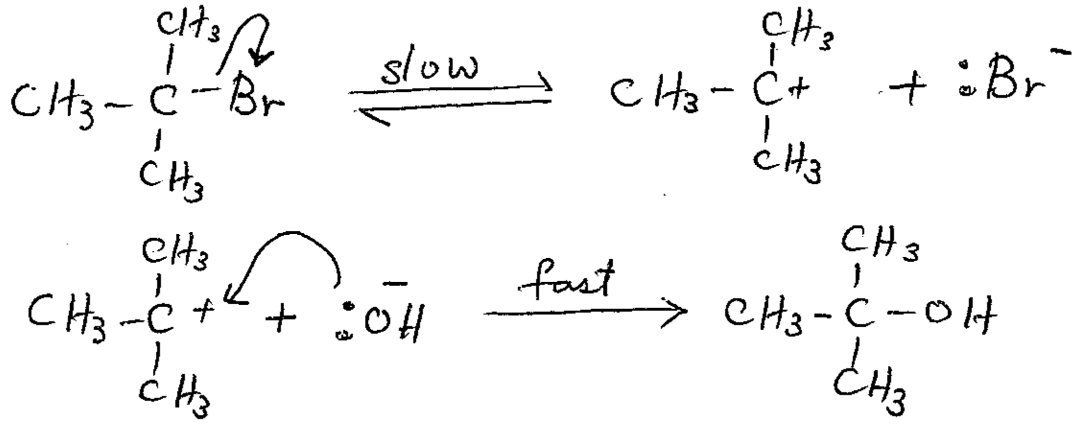
- two steps reactions: (i) $RX \rightarrow R^+ + X^-$

  (ii) $R^+ + OH^- \rightarrow ROH$

  - step (i) is slower as it involves bond breaking and thus will be the rate determining step.
  - rate depends only on $[RX]$
  - first order overall.

<u>Example.</u>

- $(CH_3)_3C-Br + OH^- \longrightarrow (CH_3)_3C-OH + Br^-$
- $rate = k[(CH_3)_3C-Br]$
  - The reaction is first order with respect to the organic compound, and zero order with respect to the hydroxide ions.
  - The concentration of the hydroxide ions isn't affecting the overall rate of the reaction.
  - The hydroxide ions must be taking part in a later fast step.
  - Increasing the concentration of the hydroxide ion will speed up the fast step, but will not have a noticeable effect on the overall rate of reaction.
  - The reaction rate is governed by the speed of the slow step.



- In this case where the slow step of the reaction is the first step, the rate equation tells you what is taking part in that slow step.

Molecularity.

The number of individual particles of the reacting species taking part in the rate determining step of a reaction.

e.g. $A + 2B \longrightarrow C + D$

molecularity is 3 - one A and two B's need to collide

$A \longrightarrow 2B$

molecularity is 1 — only one A is involved.