Chem Factsheet

www.curriculum-press.co.uk Number 240

Reconciling Mechanisms and Rates

Experimentally-derived rate equations do not simply provide us with a mathematical relationship between the concentrations of reactants and the rate at which the reaction proceeds. The form the rate equation takes also sheds light on the possible mechanism via which the reaction occurs.

The Rate Equation

This may also be referred to as the "rate law" or "rate expression" depending on the source. The equation takes the form: Rate = $k[X]^a[Y]^b[Z]^c$ where X, Y and Z are the reactants and the square brackets refer to the concentrations (measured in mol dm^{-3}) of those substances. The indices a, b and c are the **orders of the reaction** with respect to each reactant. In most exam questions these orders will take values of 0, 1 or 2, but in reality they can be non-integer values, negative values or more complex functions.

It is these orders of reaction with respect to each reactant that are critical when it comes to proposing a reaction mechanism.

Proposing a Mechanism

In most cases, you will be asked to **"suggest a mechanism that is consistent with the rate equation"**. The use of the word 'consistent' is an important one. It is not possible to predict the correct mechanism of a reaction from the rate equation alone. This is because different mechanisms may yield the same rate equation.

When proposing a mechanism you must remember the following guidelines:

1. Only ever have a maximum of **two** species reacting in any single step.
2. The **combination of all the steps proposed must be the same as the overall stoichiometric equation**. This is to say that all intermediate species must be removed by the end of the reaction.
3. The slowest / rate-determining step **(RDS) must be clearly identified**.
4. Any reactant involved in steps **up to and including the rate-determining step will be included in the rate equation**.
5. The **order of reaction** with respect to a particular reactant is **equal to the number of particles of that reactant involved up to and including the rate-determining step**.

e.g., $2X + Y \rightarrow Z$

There are four likely ways in which this reaction might proceed.

MECHANISM 1	Step 1: $X + X \rightarrow A$ RDS Step 2: $A + Y \rightarrow Z$ $\rightarrow$ Rate = $k[X]^2$ because 2 X particles are involved up to and including the RDS	MECHANISM 2	Step 1: $X + X \rightarrow A$ Step 2: $A + Y \rightarrow Z$ RDS $\rightarrow$ Rate = $k[X]^2[Y]$ because 2 X particles and 1 Y particle are involved up to and including the RDS
MECHANISM 3	Step 1: $X + Y \rightarrow B$ RDS Step 2: $B + X \rightarrow Z$ $\rightarrow$ Rate = $k[X][Y]$ because 1 X particle and 1 Y particle are involved up to and including the RDS	MECHANISM 4	Step1: $X+ Y \rightarrow B$ Step 2: $B + X \rightarrow Z$ RDS $\rightarrow$ Rate = $k[X]^2[Y]$ because 2 X particles and 1 Y particle are involved up to and including the RDS

The four different mechanisms yield three different rate equations but two mechanisms (2 & 4) yield the same rate equation. If experiments were carried out and the rate equation was determined to be Rate = $k[X]^2[Y]$, then it would not be possible to state categorically what the mechanism is, only which mechanisms were **consistent** with the rate equation.

If the rate equation was determined as Rate = $k[X][Y]$ then we could be more confident that the correct mechanism number 3. (**NB.** just because we have come up with only one mechanism that is consistent does not mean it is correct. Chemistry does some funny things; further experimental testing would be required to gather independent evidence for or against the proposed mechanism).

Worked Example

Given the data below, suggest a possible mechanism for the following reaction: $2NO + Br_2 \rightarrow 2NOBr$

Expt.	[NO] / mol dm^{-3}	[Br_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	1.2×10^{-3}	4.0×10^{-4}	1.8×10^{-2}
2	1.2×10^{-3}	8.0×10^{-4}	3.6×10^{-2}
3	3.6×10^{-3}	4.0×10^{-4}	5.4×10^{-2}

First, determine the order of reaction with respect to each reactant
Comparing experiments 1 and 2: the concentration of Br_2 doubles while the concentration of NO is unchanged. This causes the rate to double. Therefore the order with respect to Br_2 is 1.

Comparing experiments 1 and 3: the concentration of NO triples while the concentration of Br_2 is unchanged. This causes the rate to triple. Therefore the order with respect to NO is also 1.

Next, construct the rate equation: Rate = $k[NO][Br_2]$

Next, propose any possible mechanism that uses exactly one molecule of NO and exactly one molecule of Br_2 up to and including the rate-determining step, and that combines to give the overall stoichiometric equation:

e.g., $NO + Br_2 \rightarrow NOBr + Br$ RDS
$Br + NO \rightarrow NOBr$

This is not the only possible mechanism consistent with the data. The reaction could just as easily progress via:

$NO + Br_2 \rightarrow NOBr_2$ RDS
$NOBr_2 + NO \rightarrow 2NOBr$

However, it could not progress via:

$NO + NO \rightarrow N_2O_2$
$N_2O_2 + Br_2 \rightarrow 2NOBr$

even if either step was the RDS. This would mean two NO molecules were used up to and including the RDS and so the order with respect to NO would be 2 rather than 1.

> You should not concern yourself with whether or not the intermediates (e.g. $NOBr_2$ and N_2O_2) in your mechanism are likely to exist or not. You are being tested on your ability to create a mechanism consistent with the rate equation.

Nucleophilic Substitution Mechanisms

Experimentally-determined rate equations for the reactions of halogenoalkanes with hydroxide ions provide us with a better understanding as to how nucleophilic substitution occurs.
$RX + OH^- \rightarrow ROH + X^-$ ($R = C_nH_{2n+1}$; $n \geq 1$)

The reaction of a **primary** halogenoalkane (RCH_2X ; R = H or C_nH_{2n+1} ; $n \geq 1$) with hydroxide ions has the rate equation:

Rate = $k[RCH_2X][OH^-]$

The reaction of a **tertiary** halogenoalkane (R_3CX ; $R = C_nH_{2n+1}$; $n \geq 1$) with hydroxide ions has the rate equation: Rate = $k[R_3CX]$

The simple fact that two different rate equations exist, tells us that primary and tertiary halogenoalkanes must react with hydroxide ions via different mechanisms.

The rate equations also tell us that for tertiary halogenoalkanes, the rate is only dependent on the concentration of the halogenoalkane, meaning hydroxide ions must be involved **after** the RDS. However, for primary halogenoalkanes, both the halogenoalkane and hydroxide ions are involved up to and including the RDS.

Using this information, it is possible to speculate what the two mechanisms are:

Primary halogenoalkane
$RCH_2X + OH^- \rightarrow RCH_2OH + X^-$ RDS

Tertiary halogenoalkane
$R_3CX \rightarrow R_3^+ + X^-$ RDS
$R_3C^+ + OH^- \rightarrow R_3COH$

Primary halogenoalkanes react in a single bimolecular step which is called the S_N2 mechanism.

Tertiary halogenoalkanes react in a two-step mechanism in which only one species, the halogenoalkane, is involved in the RDS; this is called the S_N1 mechanism.

Note : S_N1 represents **S**ubstitution **N**ucleophilic **Uni**molecular
whilst S_N2 represents **S**ubstitution **N**ucleophilic **Bi**molecular.

Practice Questions

1. Iodine and propanone react according to the following equation: $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$
   The rate equation for this reaction is: Rate = $k[CH_3COCH_3][H^+]$

   (a) What is the order of reaction with respect to iodine?

   (b) H^+ ions do not feature in the overall stoichiometric equation but do appear in the rate equation. Suggest what this tells you about the role of H^+ in this reaction.

   (c) Propose a mechanism for the reaction consistent with the rate equation.

2. The mechanism for a reaction is proposed to be:
   $HBr + O_2 \rightarrow HOOBr$ RDS
   $HOOBr + HBr \rightarrow 2HOBr$
   $HOBr + HBr \rightarrow Br_2 + H_2O$
   $HOBr + HBr \rightarrow Br_2 + H_2O$

   (a) Determine the overall stoichiometric equation for the reaction.

   (b) Determine the rate equation for the reaction.

Answers

1 (a) Order ZERO.

(b) H^+ ions acts as a catalyst.

(c) e.g. $CH_3COCH_3 + H^+ \rightarrow CH_3COHCH_3^+$ RDS
$CH_3COHCH_3^+ + I_2 \rightarrow CH_3COCH_2I + HI + H^+$

2 (a) Add all 4 steps together and cancel the particles appearing both sides of the resulting equation to give $4HBr + O_2 \rightarrow 2Br_2 + 2H_2O$

(b) Rate = $k[HBr][O_2]$

Acknowledgements:** This Factsheet was researched and written by **Dr Chris Martin.
Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. Chemistry Factsheets** may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher. **ISSN 1351-5136