

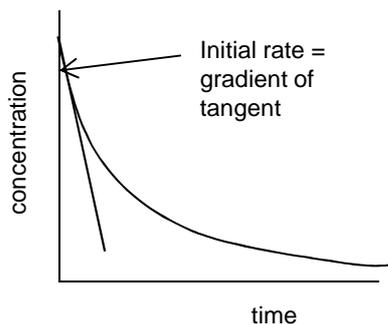
## 16. Kinetics II

The rate of reaction is defined as the **change in concentration** of a substance in **unit time**  
Its usual unit is  $\text{mol dm}^{-3}\text{s}^{-1}$

When a graph of concentration of reactant is plotted vs time, the **gradient** of the curve is the rate of reaction.

The **initial rate** is the rate at the start of the reaction where it is fastest

Reaction rates can be calculated from graphs of concentration of reactants **or** products

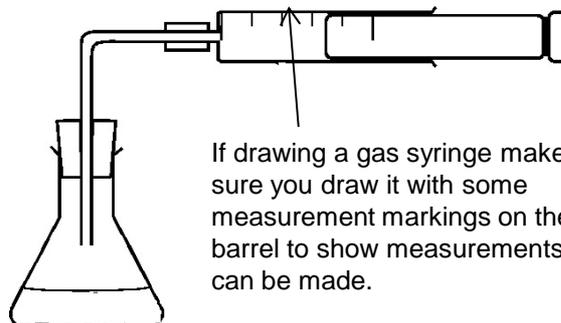
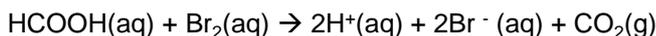
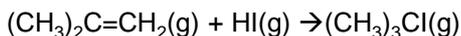


### Techniques to investigate rates of reaction

There are several different methods for measuring reactions rates. Some reactions can be measured in several ways

#### measurement of the change in volume of a gas

This works if there is a change in the number of moles of gas in the reaction. Using a gas syringe is a common way of following this.



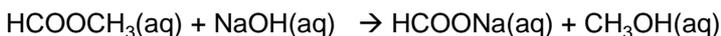
#### Measurement of change of mass

This works if there is a gas produced which is allowed to escape. Works better with heavy gases such as  $\text{CO}_2$

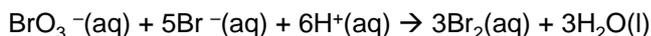


### Titrating samples of reaction mixture with acid, alkali, sodium thiosulphate etc

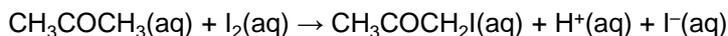
Small samples are removed from the reaction mixture, quenched (which stops the reaction) and the titrated with a suitable reagent.



The NaOH could be titrated with an acid



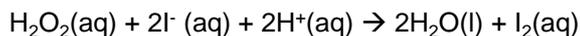
The  $\text{H}^+$  could be titrated with an alkali



The  $\text{I}_2$  could be titrated with sodium thiosulphate

### Colorimetry.

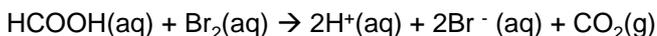
If one of the reactants or products is coloured then colorimetry can be used to measure the change in colour of the reacting mixtures



The  $\text{I}_2$  produced is a brown solution

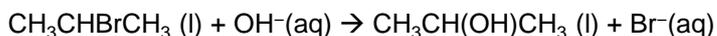
### Measuring change in electrical conductivity

Can be used if there is a change in the number of ions in the reaction mixture



### Measurement of optical activity.

If there is a change in the optical activity through the reaction this could be followed in a polarimeter



## Rate Equations

The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction,  $aA + bB \rightarrow$  products, the generalised rate equation is:  $r = k[A]^m[B]^n$

$r$  is used as symbol for rate

The unit of  $r$  is usually  $\text{mol dm}^{-3} \text{s}^{-1}$

$m, n$  are called **reaction orders**

Orders are usually integers 0,1,2

0 means the reaction is zero order with respect to that reactant

1 means first order

2 means second order

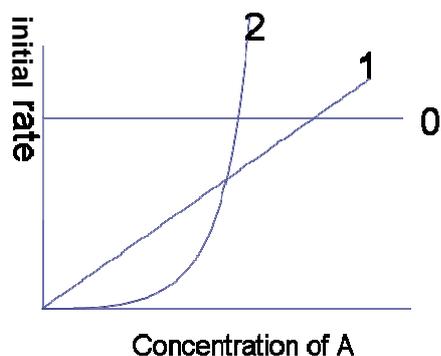
**NOTE:** the orders have *nothing* to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

The square brackets **[A]** means the concentration of A (unit  $\text{mol dm}^{-3}$ )

$k$  is called the **rate constant**

The **total order** for a reaction is worked out by adding all the individual orders together ( $m+n$ )

## Calculating orders from initial rate data



For zero order: the concentration of A has no effect on the rate of reaction  $r = k[A]^0 = k$

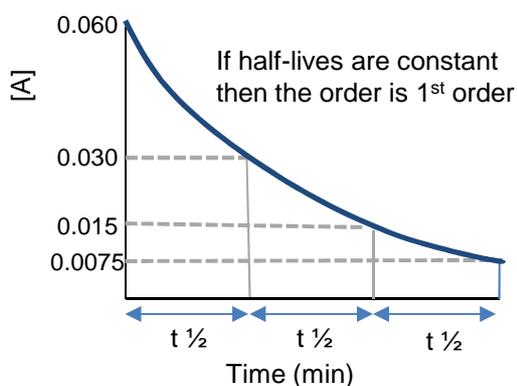
For first order: the rate of reaction is directly proportional to the concentration of A  $r = k[A]^1$

For second order: the rate of reaction is proportional to the concentration of A squared  $r = k[A]^2$

Graphs of initial rate against concentration show the different orders. The initial rate may have been calculated from taking gradients from concentration /time graphs

For a rate concentration graph to show the order of a particular reactant the concentration of that reactant must be varied whilst the concentrations of the other reactants should be kept constant.

## Continuous rate experiments



### Continuous rate data

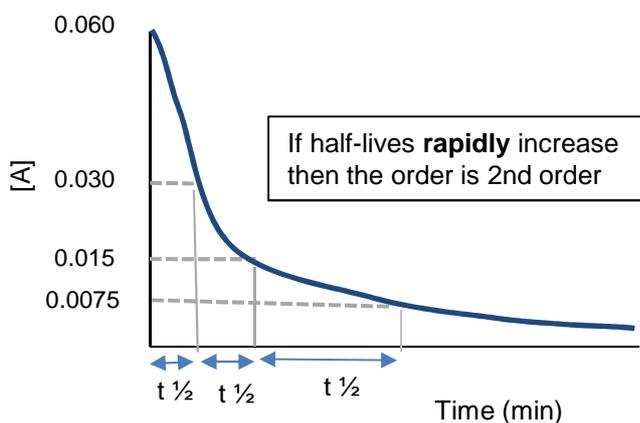
This is data from one experiment where the concentration of one substance is followed throughout the experiment.

For this method to work the concentrations of the reactants not being followed must be in large excess in the experiment so their concentrations stay virtually constant and do not affect rate.

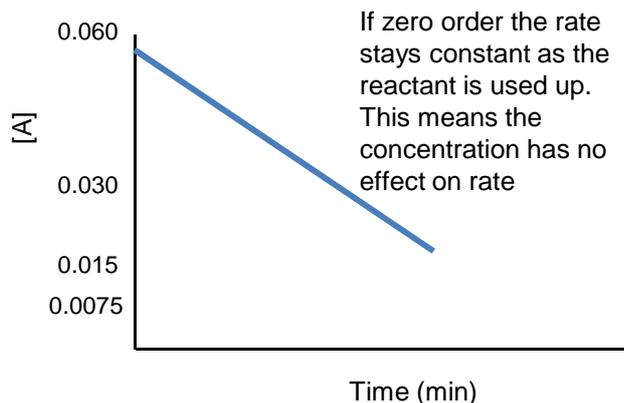
This data is processed by plotting the data and calculating successive half-lives.

The half-life of a first-order reaction is independent of the concentration and is constant

## Second order



## zero order



## The rate constant (k)

- The units of  $k$  depend on the overall order of reaction. It must be worked out from the rate equation
- The value of  $k$  is independent of concentration and time. It is constant at a fixed temperature.
- The value of  $k$  refers to a specific temperature and it **increases** if we **increase temperature**

For a 1<sup>st</sup> order overall reaction the unit of  $k$  is  **$s^{-1}$**

For a 2<sup>nd</sup> order overall reaction the unit of  $k$  is  **$mol^{-1}dm^3s^{-1}$**

For a 3<sup>rd</sup> order overall reaction the unit of  $k$  is  **$mol^{-2}dm^6s^{-1}$**

### Example (first order overall)

$$\text{Rate} = k[A][B]^0 \quad m = 1 \text{ and } n = 0$$

- reaction is first order in A and zero order in B
- overall order =  $1 + 0 = 1$
- usually written: Rate =  $k[A]$

Remember: the values of the reaction orders must be determined from experiment; they cannot be found by looking at the balanced reaction equation

#### Calculating units of $k$

- Rearrange rate equation to give  $k$  as subject

$$k = \frac{\text{Rate}}{[A]}$$

- Insert units and cancel

$$k = \frac{mol\ dm^{-3}\ s^{-1}}{mol\ dm^{-3}}$$

$$\text{Unit of } k = s^{-1}$$

**Example:** Write rate equation for reaction between A and B where A is 1<sup>st</sup> order and B is 2<sup>nd</sup> order.

$$r = k[A][B]^2 \quad \text{overall order is 3}$$

#### Calculate the unit of $k$

- Rearrange rate equation to give  $k$  as subject

$$k = \frac{\text{Rate}}{[A][B]^2}$$

- Insert units and cancel

$$k = \frac{mol\ dm^{-3}\ s^{-1}}{mol\ dm^{-3} \cdot (mol\ dm^{-3})^2}$$

- Simplify fraction

$$k = \frac{s^{-1}}{mol^2\ dm^6}$$

$$\text{Unit of } k = mol^{-2}dm^6s^{-1}$$

## Rate Equations

The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction,  $aA + bB \rightarrow$  products, the generalised rate equation is:  $r = k[A]^m[B]^n$

$r$  is used as symbol for rate

The unit of  $r$  is usually  $\text{mol dm}^{-3} \text{s}^{-1}$

$m, n$  are called **reaction orders**

Orders are usually integers 0,1,2

0 means the reaction is zero order with respect to that reactant

1 means first order

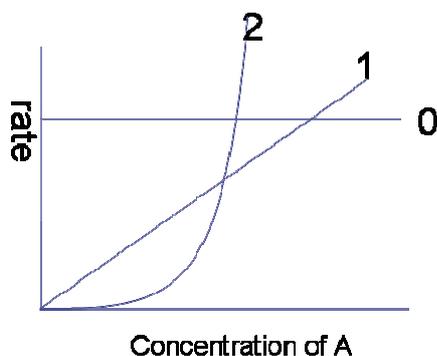
2 means second order

The square brackets **[A]** means the concentration of A (unit  $\text{mol dm}^{-3}$ )

$k$  is called the **rate constant**

**NOTE:** the orders have *nothing* to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

The **total order** for a reaction is worked out by adding all the individual orders together ( $m+n$ )



For zero order: the concentration of A has no effect on the rate of reaction  $r = k[A]^0 = k$

For first order: the rate of reaction is directly proportional to the concentration of A  $r = k[A]^1$

For second order: the rate of reaction is proportional to the concentration of A squared  $r = k[A]^2$

### The rate constant ( $k$ )

1. The units of  $k$  depend on the overall order of reaction. It must be worked out from the rate equation
2. The value of  $k$  is independent of concentration and time. It is constant at a fixed temperature.
3. The value of  $k$  refers to a specific temperature and it **increases** if we **increase temperature**

For a 1<sup>st</sup> order overall reaction the unit of  $k$  is  $\text{s}^{-1}$

For a 2<sup>nd</sup> order overall reaction the unit of  $k$  is  $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

For a 3<sup>rd</sup> order overall reaction the unit of  $k$  is  $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

### Example (first order overall)

Rate =  $k[A][B]^0$   $m = 1$  and  $n = 0$

- reaction is first order in A and zero order in B

- overall order =  $1 + 0 = 1$

- usually written: Rate =  $k[A]$

Remember: the values of the reaction orders must be determined from experiment; they cannot be found by looking at the balanced reaction equation

### Calculating units of $k$

1. Rearrange rate equation to give  $k$  as subject

$$k = \frac{\text{Rate}}{[A]}$$

2. Insert units and cancel

$$k = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol dm}^{-3}}$$

Unit of  $k = \text{s}^{-1}$

**Example:** Write rate equation for reaction between A and B where A is 1<sup>st</sup> order and B is 2<sup>nd</sup> order.

$$r = k[A][B]^2 \quad \text{overall order is 3}$$

**Calculate the unit of k**

1. Rearrange rate equation to give k as subject

$$k = \frac{\text{Rate}}{[A][B]^2}$$

2. Insert units and cancel

$$k = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol dm}^{-3} \cdot (\text{mol dm}^{-3})^2}$$

3. Simplify fraction

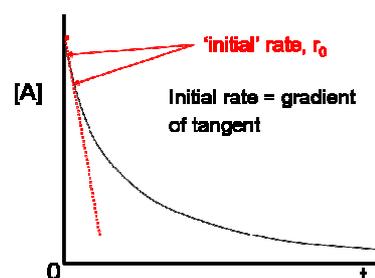
$$k = \frac{\text{s}^{-1}}{\text{mol}^2 \text{dm}^{-6}}$$

$$\text{Unit of } k = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$$

### Working out orders from experimental initial rate data

The initial rate is the rate at the start of the reaction, where it is fastest. It is often obtained by taking the gradient of the conc vs time graph.

Normally to work out the rate equation we do a series of experiments where the initial concentrations of reactants are changed (one at a time) and measure the initial rate each time. This data is normally presented in a table.



**Example:** work out the rate equation for the following reaction,  $A + B + 2C \rightarrow D + 2E$ , using the initial rate data in the table

Experiment	[A] mol dm <sup>-3</sup>	[B] mol dm <sup>-3</sup>	[C] mol dm <sup>-3</sup>	Rate mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

In order to calculate the order for a particular reactant it is easiest to compare two experiments where **only that reactant** is being changed

If conc is doubled and rate stays the same: order= 0

If conc is doubled and rate doubles: order= 1

If conc is doubled and rate quadruples : order= 2

For reactant A compare between experiments **1 and 2**

For reactant A as the concentration **doubles** (B and C staying constant) so does the rate. Therefore the order with respect to reactant **A is first order**

For reactant B compare between experiments **1 and 3** :

As the concentration of B **doubles** (A and C staying constant) the rate **quadruples**.

Therefore the order with respect to **B is 2<sup>nd</sup> order**

For reactant C compare between experiments **1 and 4** :

As the concentration of C **doubles** (A and B staying constant) the rate **stays the same**.

Therefore the order with respect to C is zero order

**The overall rate equation is  $r = k [A] [B]^2$**

The reaction is 3<sup>rd</sup> order overall and the unit of the rate constant = mol<sup>-2</sup>dm<sup>6</sup>s<sup>-1</sup>

### Working out orders when two reactant concentrations are changed simultaneously

In most questions it is possible to compare between two experiments where only one reactant has its initial concentration changed. If, however, both reactants are changed then the effect of both individual changes on concentration are multiplied together to give the effect on rate.

In a reaction where the rate equation is  $r = k [A] [B]^2$

If the [A] is x2 that rate would **x2**

If the [B] is x3 that rate would  $x3^2 = \mathbf{x9}$

If these changes happened at the same time then the rate would  $x2x9 = \mathbf{x 18}$

**Example** work out the rate equation for the reaction, between X and Y, using the initial rate data in the table

Experiment	Initial concentration of X/ mol dm <sup>-3</sup>	Initial concentration of Y/ mol dm <sup>-3</sup>	Initial rate/ mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.05	0.1	$0.15 \times 10^{-6}$
2	0.10	0.1	$0.30 \times 10^{-6}$
3	0.20	0.2	$2.40 \times 10^{-6}$

For reactant X compare between experiments **1 and 2**

For reactant X as the concentration **doubles** (Y staying constant) so does the rate. Therefore the order with respect to reactant **X is first order**

Comparing between experiments 2 and 3 :

Both **X and Y double** and the **rate goes up by 8**

We know X is first order so that will have doubled rate

The effect of Y, therefore, on rate is to have quadrupled it.

**Y must be second order**

**The overall rate equation is  $r = k [X] [Y]^2$**

The reaction is 3<sup>rd</sup> order overall and the unit of the rate constant = mol<sup>-2</sup>dm<sup>6</sup>s<sup>-1</sup>

### Calculating a value for k using initial rate data

Using the above example, choose any one of the experiments and put the values into the rate equation that has been rearranged to give k. Using experiment 3:

$$r = k [X] [Y]^2 \longrightarrow k = \frac{r}{[X] [Y]^2} \quad k = \frac{2.40 \times 10^{-6}}{0.2 \times 0.2^2} \quad k = \mathbf{3.0 \times 10^{-4} \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}}$$

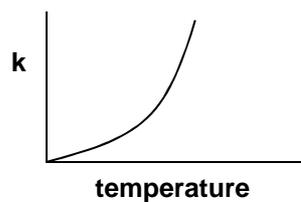
**Remember k is the same for all experiments done at the same temperature.**

**Increasing the temperature increases the value of the rate constant k**

## Effect of Temperature on rate constant

### Increasing the temperature increases the value of the rate constant $k$

Increasing temperature increases the rate constant  $k$ . The relationship is given by the Arrhenius equation  $k = Ae^{-E_a/RT}$  where  $A$  is a constant  $R$  is gas constant and  $E_a$  is activation energy.

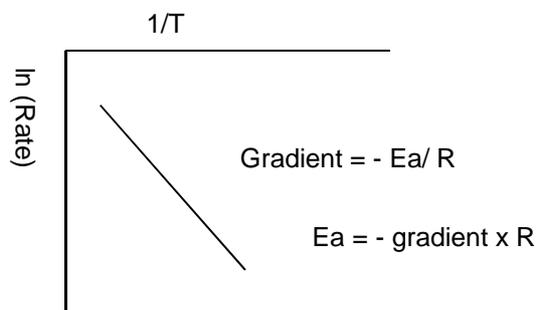


The Arrhenius equation can be rearranged

$$\ln k = \text{constant} - E_a/(RT)$$

$k$  is proportional to the rate of reaction so  $\ln k$  can be replaced by  $\ln(\text{rate})$

From plotting a graph of  $\ln(\text{rate})$  or  $\ln k$  against  $1/T$  the activation energy can be calculated from measuring the gradient of the line



## Rate Equations and mechanisms

A mechanism is a series of steps through which the reaction progresses, often forming intermediate compounds. If all the steps are added together they will add up to the overall equation for the reaction

Each step can have a different rate of reaction. The slowest step will control the overall rate of reaction. **The slowest step is called the rate-determining step.**

The molecularity (number of moles of each substance) of the molecules in the slowest step will be the same as the order of reaction for each substance.

e.g. 0 moles of A in slow step would mean A is zero order.

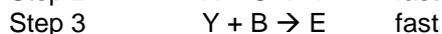
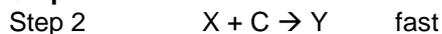
1 mole of A in the slow step would mean A is first order

### Example 1

#### overall reaction



#### Mechanism



$$r = k [A]^1 [B]^1 [C]^0$$

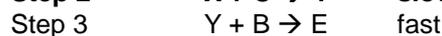
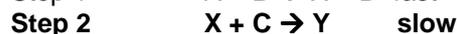
C is zero order as it appears in the mechanism in a fast step after the slow step

### Example 2

#### overall reaction

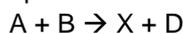


#### Mechanism



$$r = k [X]^1 [C]^1$$

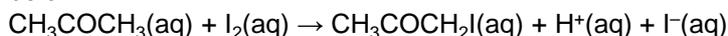
The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step



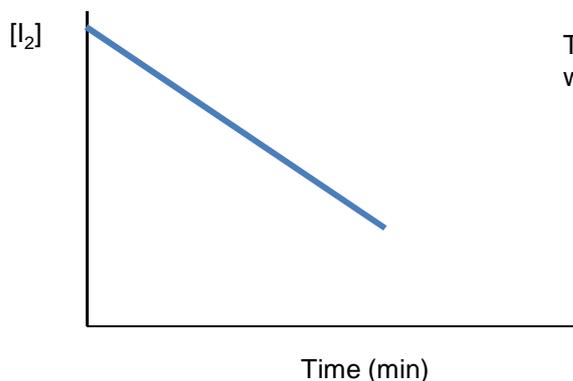
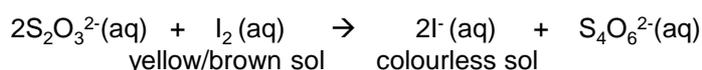
$$r = k [A]^1 [B]^1 [C]^1$$

## Investigating the rate of reaction between iodine and propanone

Propanone reacts with iodine in acidic solution (the acid is a catalyst) as shown in the equation below.



This reaction can be followed by removing small samples from the reaction mixture with a volumetric pipette. The sample is then quenched by adding excess sodium hydrogencarbonate to neutralize acid catalyst which stops the reaction. Then the sample can be titrated with sodium thiosulphate using a starch catalyst



This reaction is zero order with respect to  $\text{I}_2$  but 1<sup>st</sup> order with respect to the propanone and acid catalyst

The rate equation for the reaction is

$$\text{Rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})]$$

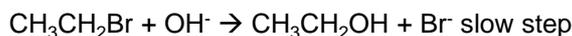
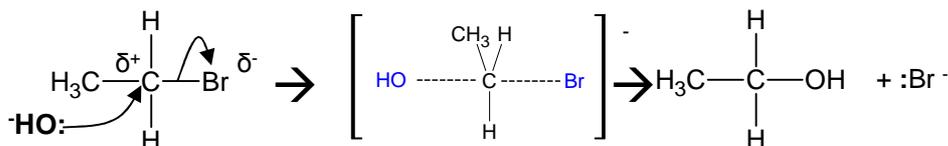
If there is a zero order reactant there must be at least two steps in the mechanism because the rate determining step will not involve the zero order reactant

The rate determining step of this reaction must therefore contain one propanone molecule and one  $\text{H}^+$  ion forming an intermediate. The iodine will be involved in a subsequent faster step.

Example 3: S<sub>N</sub>1 or S<sub>N</sub>2?

Remember the nucleophilic substitution reaction of halogenoalkanes and hydroxide ions.

This is a one step mechanism



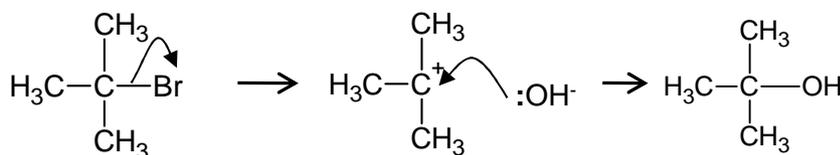
The rate equation is

$$r = k [\text{CH}_3\text{CH}_2\text{Br}] [\text{OH}^-]$$

This is called S<sub>N</sub>2.  
Substitution, Nucleophilic,  
2 molecules in rate  
determining step

Primary halogenoalkanes tend to  
react via the SN2 mechanism

**SN<sub>1</sub> nucleophilic substitution mechanism for tertiary halogenoalkanes**



The Br first breaks away  
from the haloalkane to  
form a carbocation  
intermediate

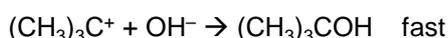
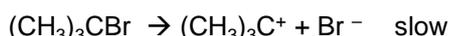
The hydroxide  
nucleophile then attacks  
the positive carbon

Tertiary halogenoalkanes  
undergo this mechanism as the  
tertiary carbocation is made  
stabilised by the electron  
releasing methyl groups around it.  
(see alkenes topic for another  
example of this).  
Also the bulky methyl groups  
prevent the hydroxide ion from  
attacking the halogenoalkane in  
the same way as the mechanism  
above

Overall Reaction



Mechanism:



The rate equation is

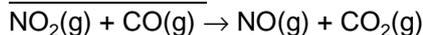
$$r = k [(\text{CH}_3)_3\text{CBr}]$$

This is called S<sub>N</sub>1.  
Substitution, Nucleophilic,  
1 molecule in rate  
determining step

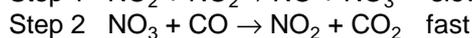
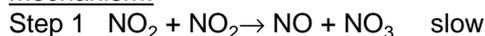
Primary halogenoalkanes don't do the SN<sub>1</sub> mechanism  
because they would only form an unstable primary  
carbocation.

Example 4

Overall Reaction



Mechanism:



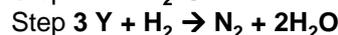
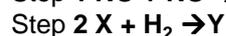
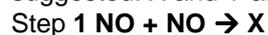
• NO<sub>3</sub> is a reaction intermediate

NO<sub>2</sub> appears twice in the slow steps so it  
is second order. CO does not appear in  
the slow step so is zero order.

$$r = k [\text{NO}_2]^2$$

Example 5

Using the rate equation  $\text{rate} = k[\text{NO}]^2[\text{H}_2]$  and  
the overall equation  $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ , the  
following three-step mechanism for the reaction was  
suggested. X and Y are intermediate species.



Which **one of the three steps is the rate-determining step?**

Step 2 – as H<sub>2</sub> appears in rate equation and  
combination of step 1 and 2 is the ratio that  
appears in the rate equation.