The hydrolysis of 2-bromo-2-methylpropane

A simple kinetic study of this hydrolysis reaction shows that it follows an S_N1 mechanism

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When teaching halogenoalkanes, it is usually stated that primary halides hydrolyse by the S_N2 mechanism, tertiary halides by the S_N1 mechanism and secondary halides by a mixture of both. Students are often confused because the S_N1 reaction takes place in **two** steps while the S_N2 mechanism has just **one** step.

S_N1 reactions

Slow, rate determining step

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$

Fast step

$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$

The first step is slow because it involves bond breaking, while the second step is rapid because it involves the attraction of oppositely charged ions. The reaction is *unimolecular* (hence the '1' in S_N1) because only **one** species is involved in the rate determining step.

S_N2 reactions

Slow, rate determining step

$C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$

This step is slow because it involves bond breaking. The reaction is *bimolecular* (hence the '2' in S_N2) because **two** species are involved in the slow step.

Rate equations

At an introductory level, kinetic evidence is used to decide which mechanism is operating. There are two different rate equations for the two mechanisms.

$$S_N1: \quad \text{rate} = k[\text{RBr}]^1[\text{OH}^-]^0$$
$$S_N2: \quad \text{rate} = k[\text{RBr}]^1[\text{OH}^-]^1$$

In short

- Students determine the order of the reaction with respect to both OH^- ions and 2-bromo-2-methylpropane
- Students should be able to complete the experiments and obtain their results in one hour

Students will appreciate that derivation of the rate equation enables them to decide which mechanism is operating. This formed the basis for a recent A2 level question[1] on the hydrolysis of tertiary butyl bromide (2-bromo-2-methylpropane) in the presence of sodium hydroxide. This reaction is often cited as a classic example of a S_N1 reaction.

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

Confirming the mechanism

The following experiments are designed to confirm this mechanism by determining the order with respect to both OH^- ions and 2-bromo-2-methylpropane. Several methods can be used for such a kinetic study. We used the initial rates method.

A small quantity of sodium hydroxide is added to a large excess of 2-bromo-2-methylpropane in the presence of a few drops of phenolphthalein. As the reaction proceeds, the OH^- ions are used up and the pink colour of the phenol phenolphthalein disappears. The 2-bromo-2-methylpropane is in such large excess that its concentration may be considered to be virtually constant.

Because we are only looking at the early stages of the reaction, the concentration/time graph (*fig 1*) is almost a straight line. This means that the rate of the reaction is approximately [OH$^-$] divided by the time taken for it to be used up, that is when the pink colour of the phenolphthalein disappears. The concentrations of the reactants are adjusted so that the time for the pink colour to disappear is about a minute.

This means that a whole series of experiments can be carried out in just over an hour and the order with respect to both the [OH$^-$] and [t-butylbromide] can easily be found. It is not possible to obtain both orders in this time using other methods (for example titration) because they take so much longer to complete.

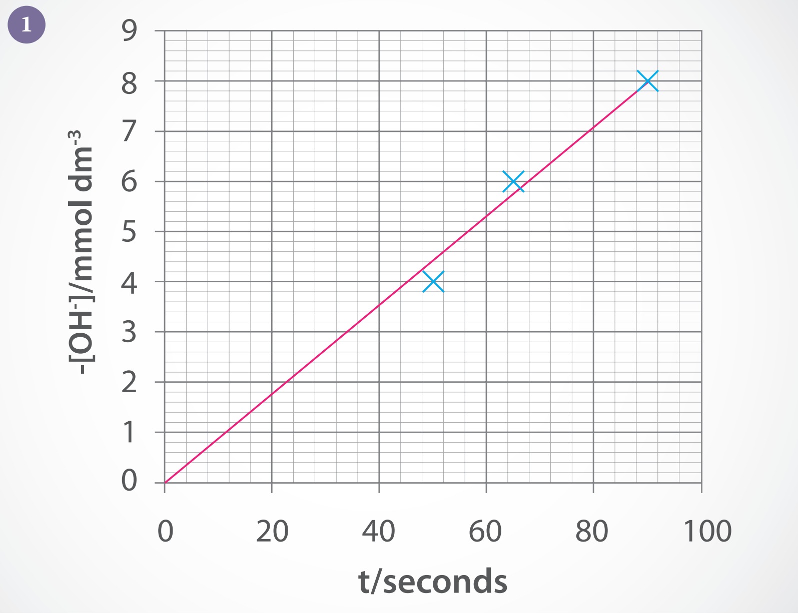

Fig 1
A graph showing how [OH$^-$] varies with time

Experiment 1: To determine the order with respect to OH$^-$ ions

The rate of the reaction is found by adding t-butylbromide to known small amounts of NaOH in the presence of phenolphthalein. The initial rate is found by measuring the time for the pink colour to disappear.

The solvent is 80/20 propanone/water by volume, in which both the NaOH and the bromide are soluble. No attempt was made to thermostat the solutions, but they were allowed to stand for half an hour to take on the temperature of the laboratory.

Kit

Each group will need the following

- 2 burettes
- 30 cm^3 of 80/20 propanone/water by volume
- 50 cm^3 of 0.01 mol dm^{-3} NaOH in the same solvent. This solution should be freshly made as it deteriorates on standing.
- Specimen tube
- Stop clock
- 2 cm^3 phenolphthalein
- 5 cm^3 2-bromo-2- methylpropane. This should be from a new bottle as an old bottle hydrolyses on standing
- 1.0 cm^3 calibrated pipette (preferably the blow out type) and filler

In all experiments the total volume made is 10.0 cm^3. As 0.50 cm^3 of the bromide and 0.10 cm^3 of phenolphthalein are used, the volume of NaOH solution and solvent must be 9.40 cm^3.

Procedure

1. Using burettes, add 3.40 cm^3 of solvent to 6.0 cm^3 of the NaOH solution, placed in the specimen tube.
2. Add two drops of phenolphthalein.
3. Add 0.50 cm^3 of the bromide from the pipette and start the stop clock.
4. Record the time, *t*, for the pink colour to just disappear.

Results

The initial rate is
(6.0 x 0.01)/(10.0 x *t*) mol dm^{-3} s^{-1}.

Repeat the experiment using first 4.0 cm^3 and then 8.0 cm^3 of the NaOH solution, adding 5.40 cm^3 and 1.40 cm^3 of solvent to keep the total volume to 10.0 cm^3.

A typical set of results is shown in *figs 1 and 2. Fig 1* shows that a plot of [OH$^-$] (that is –[OH$^-$]) against time is straight line passing through the origin. Students often incorrectly think that such a graph shows first order kinetics, but if they are told to think about how the **rate** varies with [OH$^-$] (as shown in *fig 2*) they will see that it the results show that the reaction is zero order with respect to OH$^-$ ions.

Experiment 2: To determine the rate with respect to 2-bromo-2-methylpropane

The experiment is then repeated, keeping [NaOH] constant but varying [Br–]. In each experiment, keep [NaOH] constant by using 6.0 cm^3 of the NaOH solution. Do four

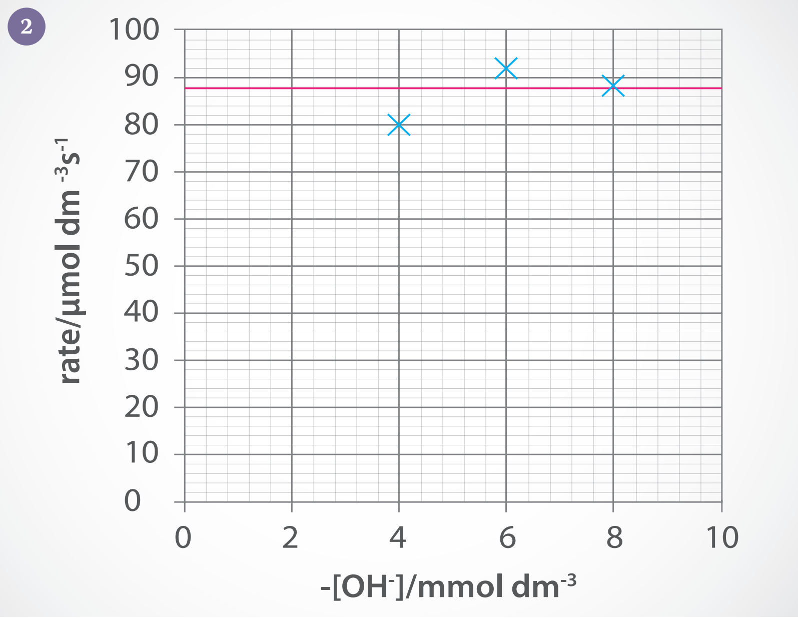

Fig 2
Constant rates show that the reaction is zero order with respect to [OH$^-$]

experiments using 0.40 cm^3, 0.60 cm^3, 0.70 cm^3 and 0.80 cm3 of 2-bromo-2-methylpropane. The solvent added must 3.50 cm^3, 3.30 cm^3, 3.20 cm^3 and 3.1 cm^3 in order to keep the total volume to 10.0 cm^3.

Results

The initial rates are calculated in the same way as in the previous experiments.The initial rates increase as the amount of bromide was increased and this observation suggests that the reaction is first order with respect to [Br^-].

To confirm this dependence, draw a graph of rate against [Br^-], including the origin and the point with 0.5 cm^3 of bromide added from the earlier experiment. The actual values of [Br^-] can be calculated knowing that the concentration of pure 2-bromo-2-methylpropane is 9.2 mol dm^{-3}.

A fairly good straight line graph is obtained with a slope equal to the rate constant for the reaction. A typical set of results is shown in *fig 3*.

Health and safety precautions

Propanone, 2-bromo-2-methylpropane and phenolphthalein are all highly flammable and propane is irritating to the eyes. Keep the sodium hydroxide solution in a stoppered bottle in-between runs. There must be no flames in the laboratory which must be adequately ventilated.

Optional extra

With a good class it can be pointed out that the results obtained from the previous experiments do not necessarily show that the reaction is S_N1 because it could be following a S_N2 mechanism with water acting as the nucleophile. The water is in such large excess that it does not vary in the course of the reaction. Such a reaction is said to show *pseudo-first-order* kinetics.

Slow rate determining step

$$(CH_3)_3CCBr + H_2O \rightarrow (CH_3)_3COH_2^+ + Br^-$$

Rapid neutralisation

$$(CH_3)_3COH_2^+ + OH^- \rightarrow (CH_3)_3COH + H_2O$$

The classic way to distinguish S_N1 from S_N2 is by the common ion effect.[2] The S_N1 mechanism may be written as follows:

Slow reversible rate determining step

$$RBr \rightarrow R^+ + Br^-$$

Rapid ionic reaction

$$R^+ + OH^- \rightarrow ROH$$

If Br^- ions are added, the equilibrium in the first step is shifted to the left by the common ion effect. As a result, the reaction slows down. Unfortunately the addition of ionic salts speeds up the reaction by increasing the polarity of the medium.

Control

To compensate for this increase in polarity, a control experiment must be carried out using a salt that does not affect the equilibrium position. Such a salt must contain an anion which is a poorer nucleophile than the Br^- ion. Many anions are poorer nucleophiles than the Br^- ion including the Cl^- ion. We used LiCl, rather than NaCl, as the source of Cl^- ions because it is much more soluble in 80/20 propanone/water than NaCl. In the same solvent NaBr is more soluble than LiBr, so we used NaBr as the source of Br^- ions.

Experiment 3: The common ion effect

1. Dissolve 0.43 g (0.01 moles) of LiCl (a harmful solid) in 10 cm^3 of water and then add 40 cm^3 of propanone.

2. Make a similar solution using 1.03 g of NaBr.

3. To 9.4 cm^3 of these solutions add two drops of phenolphthalein and 0.50 cm^3 of 2-bromo-2-methylpropane.

Compare the rates with a tube that contained no added LiCl or NaBr. We found that the rate with LiCl was faster (67 seconds) than with no added salt (96 seconds), but the rate with NaBr (82 seconds) was slower than with LiCl.

Conclusions

Two conclusions can be drawn from these results.

1. The addition of salts speeds up the reaction. This is characteristic of a reaction which involves separation of charges of opposite sign in the transition state.[3]

2. The addition of Br^- ions slows down the reaction.

No conclusion about the mechanism can be drawn from the first observation as both the S_N1 and S_N2 mechanisms have transition states with separated charges of opposite sign.[2] The slowing down of the reaction on the addition of Br^- ions gives strong support for the S_N1 mechanism. The S_N2 mechanism is excluded if we assume that the second step is so fast that the reverse of the first reaction has not enough time to take place. This is a reasonable assumption but does not constitute a proof. Better evidence is provided if the more detailed kinetic study is done.[4]

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Peter Hughes has recently retired from Westminter School where he supervised sixth form research. Miles Huseyin is reading biochemistry at St Catherine's College, Oxford and Younis Porteous is reading natural sciences at Trinity Hall, Cambridge.

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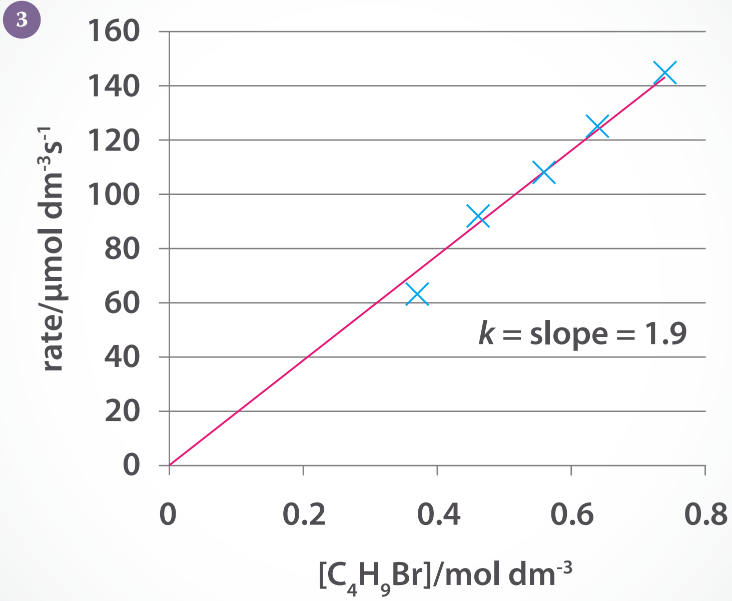

Fig 3

Plotting the rate of the reaction against [C_4H_9Br] gives a straight line. The slope is equal to the rate constant, *k*.