Mechanisms of hydrolysis reactions of haloalkanes

A group of students investigated whether the structure of a haloalkane affects the rate equation and mechanism for a substitution reaction.

They studied the rate of hydrolysis of the tertiary haloalkane, 2-bromo-2-methylpropane and the primary haloalkane, 1-bromobutane using hydroxide ions.

Method 1: The hydrolysis of 2-bromo-2-methylpropane, $CH_3C(CH_3)BrCH_3$

Equal moles of 2-bromo-2-methylpropane and sodium hydroxide in solution were mixed at room temperature. At the start of the reaction a sample was withdrawn and the reaction in the sample was quenched (slowed down or stopped). The concentration of hydroxide in the sample was determined by titration. The sampling and quenching procedure was repeated every 5 minutes as the reaction proceeded. The results are shown in **Table 4.1**.

Time / min	$[OH^-] \times 10^{-3}$ / mol dm^{-3}
0	50.0
5	30.0
10	19.5
15	12.0
20	9.0
25	5.0
30	4.5

Table 4.1

Method 2: The hydrolysis of 1-bromobutane, $CH_3CH_2CH_2CH_2Br$

The initial concentrations of 1-bromobutane and sodium hydroxide were changed as in **Table 4.2**. The initial rate of reaction was measured for each mixture.

Mixture number	$[C_4H_9Br] \times 10^{-1}$ / mol dm^{-3}	$[OH^-] \times 10^{-1}$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.25	0.10	3.2×10^{-6}
2	0.50	0.10	6.5×10^{-6}
3	0.50	0.50	3.3×10^{-5}

Table 4.2

Research by the students found there were two possible mechanisms for this type of substitution reaction.

Either: $C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$ (**mechanism A**)

Or: $C_4H_9Br \rightleftharpoons C_4H_9^+ + Br^-$ **followed by** $C_4H_9^+ + OH^- \rightarrow C_4H_9OH$ (**mechanism B**)

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