

- 7.51 The following alkyl chlorides undergo first-order nucleophilic substitution by water (solvolysis) with dramatically different rates. The first-order reaction rates were measured for the following alkyl chlorides using water-dioxane mixtures as the solvent system.

		relative rate
chloroethoxymethane 1-	$\text{Cl}-\text{CH}_2\text{OCH}_2\text{CH}_3$	$1 \times 10^9$
chlorobutane	$\text{Cl}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1
<b>1-chloro-2-methoxyethane</b>	<b><math>\text{Cl}-\text{CH}_2\text{CH}_2\text{OCH}_3</math></b>	0.2

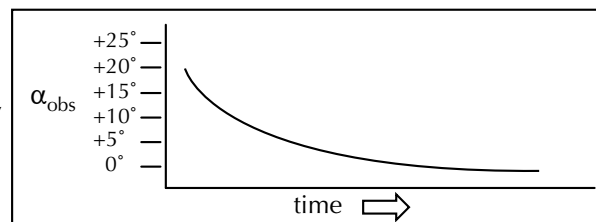
- (a) Write the mechanism for the rate-determining step of the reaction of chloroethoxymethane.

- (b) Using words and drawings, explain the relative rates for these three compounds.

- 7.52 The specific rotation of (*S*)-2-bromopentane in ethanol is  $[\alpha]_{\text{D}} +31^\circ$ . The optical activity of a solution of (*S*)-2-bromopentane with an observed rotation ( $\alpha_{\text{obs}}$ ) of  $+20^\circ$  is monitored, and it remains unchanged until sodium bromide is added to the solution.

Experiment A:

When a 0.10 M solution of sodium bromide is added to a solution of (*S*)-2-bromopentane, the initially observed rotation gradually decreases until the solution is optically inactive (shown to the right). Analysis of the solution at any point along the way indicates that only sodium bromide and 2-bromopentane are present.



Experiment B:

A 0.25 M solution of sodium bromide is used. No other experimental conditions are changed.

- (a) On the graph above, add the curve for the change in observed rotation over time that is anticipated from Experiment B.
- (b) Using words and drawings, explain the original experimental result and the rationale behind your prediction about Experiment B.

- (c) Only one of these statements explains why the solution becomes optically inactive. Which one is it?

- All the starting material is irreversibly converted to the product.
- One-half of the starting material is irreversibly converted to the product.
- The starting material is reversibly converted to the product.