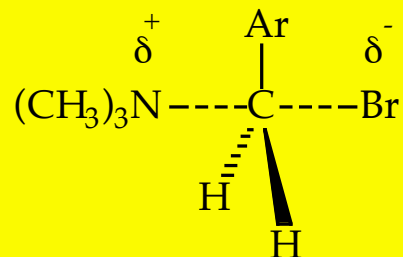


Testing a Mechanism: Reaction Kinetics

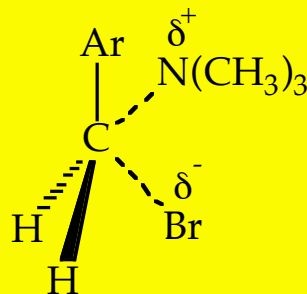
Case I



Plausible Mechanism: A one step reaction proceeding through the transition state shown below :

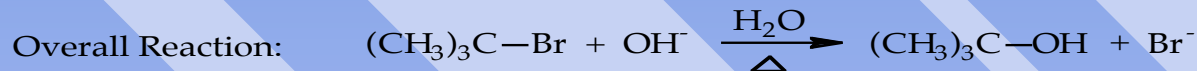


Question: How can one rule out the following transition state?

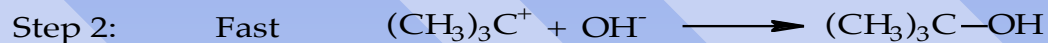
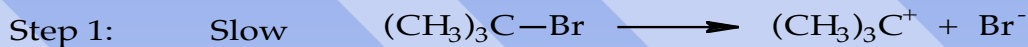


Testing a Mechanism: Reaction Kinetics

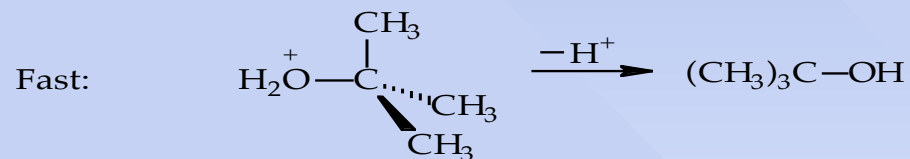
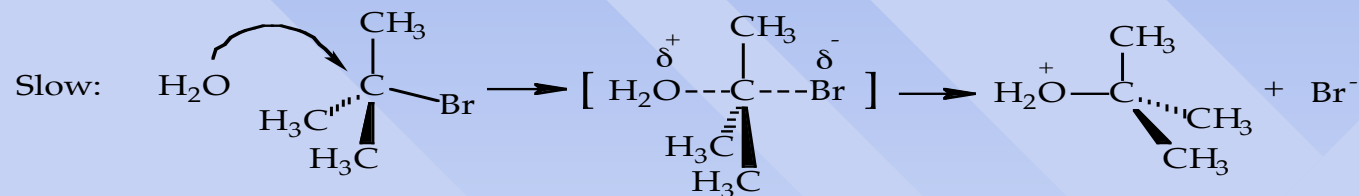
Case II



Plausible Mechanism:



Question: Is the mechanism shown below, which is also consistent with first order kinetics, as plausible as the mechanism shown above?

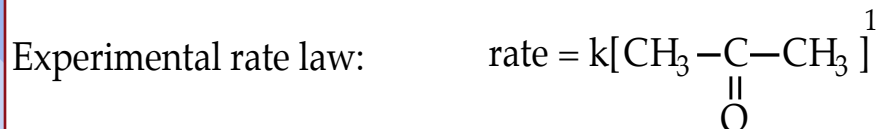
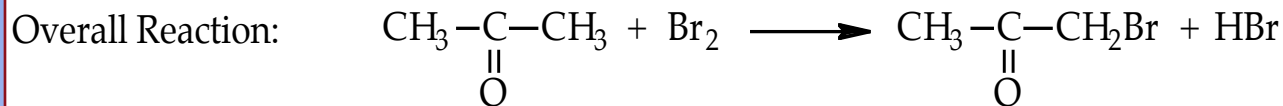


$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]^1 [\text{H}_2\text{O}]^1 \quad \text{But } [\text{H}_2\text{O}] \cong \text{constant}$$

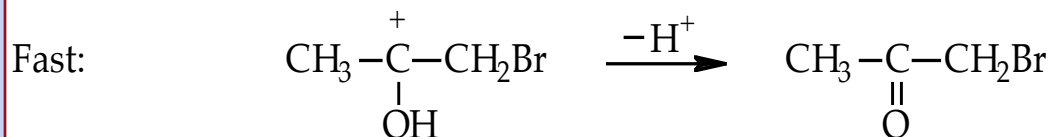
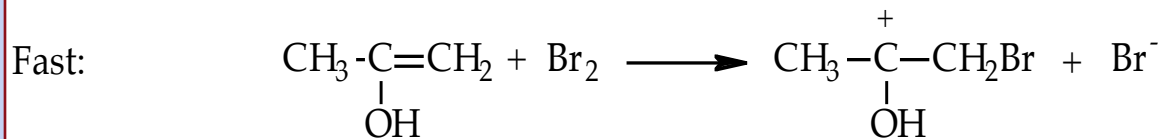
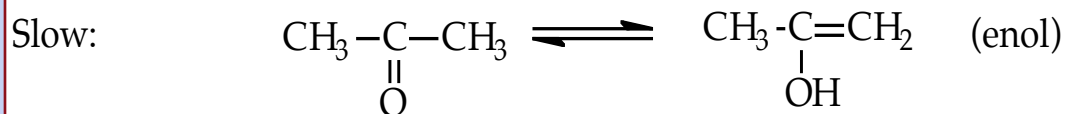
$$\therefore \text{rate} = k'[(\text{CH}_3)_3\text{CBr}]^1$$

Testing a Mechanism: Reaction Kinetics

Case III



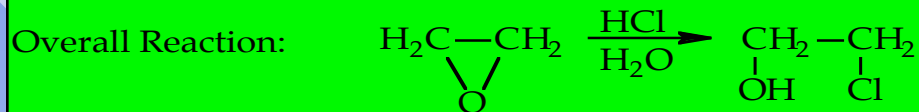
Plausible Mechanism:



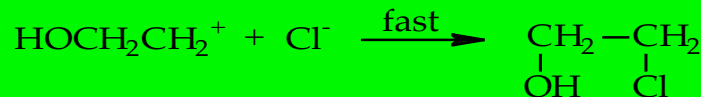
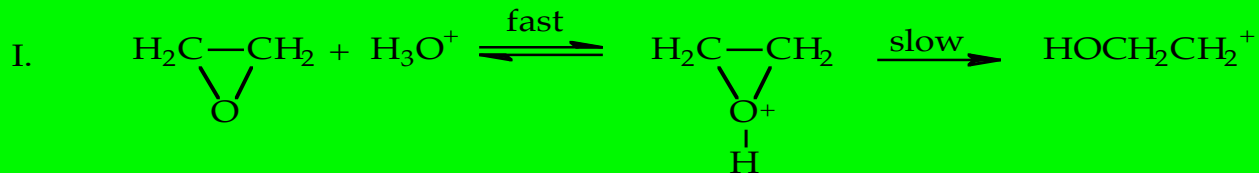
Rationale: Whenever the experimental rate law is independent of the concentration of an obvious reactant species, one which is not present in large excess, a multi-step reaction is probably occurring, and at least one reaction intermediate is implicated.

TESTING A MECHANISM: REACTION KINETICS

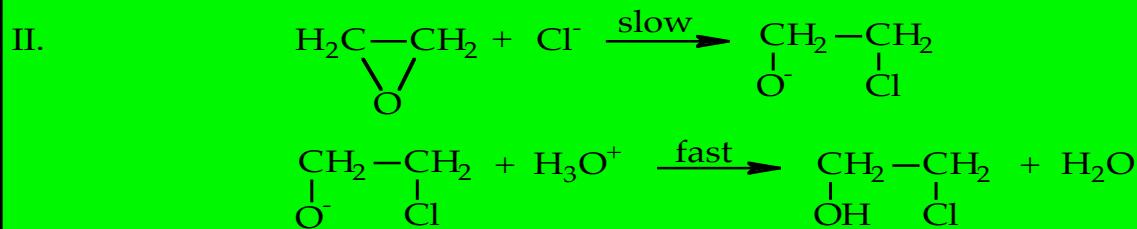
CASE IV



Possible Mechanisms:



$$\text{rate} = k[\text{H}_2\text{C}-\text{CH}_2]_{\text{O}^+\text{H}}^1 = kK[\text{H}_2\text{C}-\text{CH}_2]_{\text{O}}^1 [\text{H}_3\text{O}^+]^1 = k'[\text{H}_2\text{C}-\text{CH}_2]_{\text{O}}^1 [\text{H}_3\text{O}^+]^1$$



$$\text{rate} = k[\text{H}_2\text{C}-\text{CH}_2]_{\text{O}}^1 [\text{Cl}^-]^1$$

Experimentally determined rate law:
$$\text{rate} = k[\text{H}_2\text{C}-\text{CH}_2]_{\text{O}}^1 [\text{H}_3\text{O}^+]^1 [\text{Cl}^-]^1$$

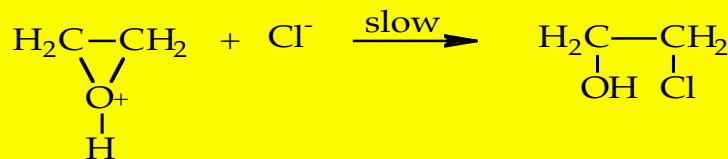
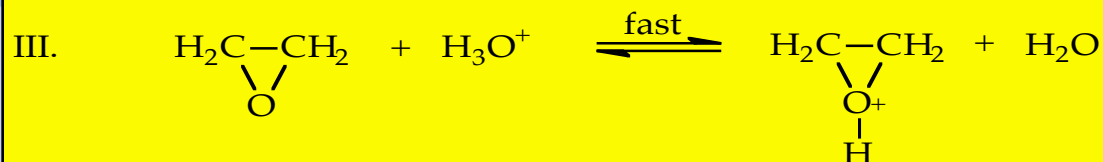
TESTING A MECHANISM: REACTION KINETICS

CASE IV CONTINUED

Point of Information: Based on the experimentally derived rate law, one might wish to propose a pathway whose slow step proceeds via a transition state involving epoxide, hydronium ion, and chloride ion. Unfortunately, three-body collisions are low probability events and are not very likely.

A more plausible explanation to account for third order kinetics involves a rapid equilibrium step prior to the slow step in the mechanism.

Most Plausible Mechanistic Pathway:



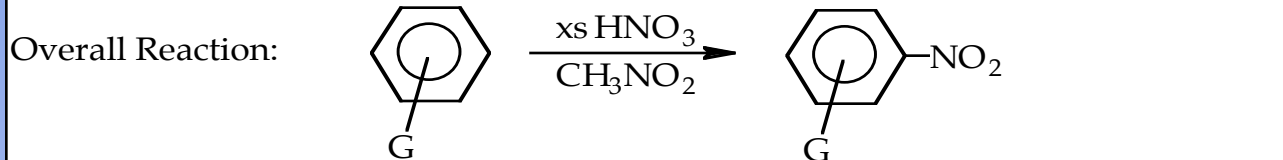
$$\text{rate} = k \left[\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \diagdown \quad / \\ \text{O}^+ \\ | \\ \text{H} \end{array} \right]^1 [\text{Cl}^-]^1 \quad \text{But:} \quad \left[\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \diagdown \quad / \\ \text{O}^+ \\ | \\ \text{H} \end{array} \right]^1 = \frac{K \left[\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \diagdown \quad / \\ \text{O} \end{array} \right]^1 [\text{H}_3\text{O}^+]^1}{[\text{H}_2\text{O}]^1}$$

$$\therefore \text{rate} = k \frac{K \left[\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \diagdown \quad / \\ \text{O} \end{array} \right]^1 [\text{H}_3\text{O}^+]^1}{[\text{H}_2\text{O}]^1} [\text{Cl}^-]^1 \quad \text{where } [\text{H}_2\text{O}]^1 \cong \text{constant}$$

$$\text{and} \quad \text{rate} = k' \left[\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \diagdown \quad / \\ \text{O} \end{array} \right]^1 [\text{H}_3\text{O}^+]^1 [\text{Cl}^-]^1$$

Testing a Mechanism: Reaction Kinetics

Case V

Overall Reaction: 

Observation: For benzene and benzene derivatives with electron donating substituents, the rates of nitration under the above conditions are identical. When chlorobenzene and benzene derivatives with electron withdrawing substituents undergo nitration under the above conditions, the rates of nitration of the latter differ from that of the former and from one another.

Rationale:

Step 1: $2 \text{HNO}_3 \xrightleftharpoons{\text{fast}} \text{H}_2\text{NO}_3^+ + \text{NO}_3^-$

Step 2: $\text{H}_2\text{NO}_3^+ \longrightarrow \text{NO}_2^+ + \text{H}_2\text{O}$

Step 3: $\text{NO}_2^+ + \text{ArH} \longrightarrow \left[\text{Ar} \begin{array}{l} \text{NO}_2 \\ \text{H} \end{array} \right]^+$

Step 4: $\left[\text{Ar} \begin{array}{l} \text{NO}_2 \\ \text{H} \end{array} \right]^+ + \text{NO}_3^- \longrightarrow \text{ArNO}_2 + \text{HNO}_3$

Scenarios:

For "activated" benzenes, Step 2 is slow and:

$$\text{rate} = k[\text{H}_2\text{NO}_3^+]^1 = k' \frac{[\text{HNO}_3]^2}{[\text{NO}_3^-]^1} \quad \text{nearly a constant value independent of } [\text{ArH}]$$

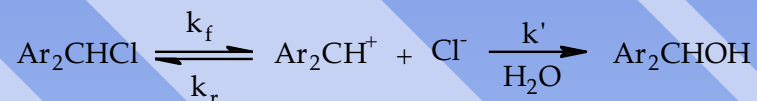
For "deactivated" benzenes, Step 3 is slow and:

$$\text{rate} = k[\text{NO}_2^+]^1 [\text{ArH}]^1 \quad \text{reaction rate dependent upon } [\text{ArH}]$$

Testing a Mechanism: Reaction Kinetics

Case VI

Consider the following reaction sequence:



Experimentally determined rate law for the above hydrolysis:

$$\text{rate} = \frac{k_f [\text{Ar}_2\text{CHCl}]^1}{\frac{k_r}{k''} [\text{Cl}^-]^1 + 1}$$

Question: How is the rate expression derived?

Answer: **Steady-State Assumption Technique**

Assume that the concentration of a reactive intermediate in a mechanistic pathway equals zero. In the above reaction pathway:

$$\frac{d[\text{Ar}_2\text{CH}^+]}{dt} = 0 = \text{rate of formation} - \text{rate of destruction}$$

$$\frac{d[\text{Ar}_2\text{CH}^+]}{dt} = 0 = k_f [\text{Ar}_2\text{CHCl}]^1 - \left[k_r [\text{Ar}_2\text{CH}^+]^1 [\text{Cl}^-]^1 + k' [\text{Ar}_2\text{CH}^+]^1 [\text{H}_2\text{O}]^1 \right]$$

$$k_f [\text{Ar}_2\text{CHCl}]^1 = \left[k_r [\text{Ar}_2\text{CH}^+]^1 [\text{Cl}^-]^1 + k' [\text{Ar}_2\text{CH}^+]^1 [\text{H}_2\text{O}]^1 \right]$$

$$k_f [\text{Ar}_2\text{CHCl}]^1 = [\text{Ar}_2\text{CH}^+]^1 \left[k_r [\text{Cl}^-]^1 + k'' \right]$$

$$[\text{Ar}_2\text{CH}^+]^1 = \frac{k_f [\text{Ar}_2\text{CHCl}]^1}{k_r [\text{Cl}^-]^1 + k''}$$

But the rate of product formation is: $\text{rate} = k' [\text{Ar}_2\text{CH}^+]^1 [\text{H}_2\text{O}]^1 = k'' [\text{Ar}_2\text{CH}^+]^1$

$$\therefore \text{rate}_{\text{prod. form.}} = k'' \frac{k_f [\text{Ar}_2\text{CHCl}]^1}{k_r [\text{Cl}^-]^1 + k''} = \frac{k_f [\text{Ar}_2\text{CHCl}]^1}{\frac{k_r}{k''} [\text{Cl}^-]^1 + 1}$$

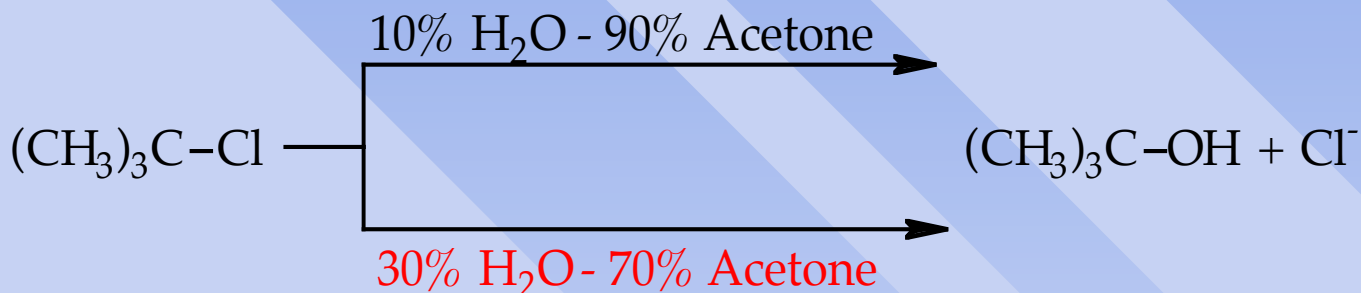
Kinetic Salt Effects

- **Ionic Strength**
- **Common Ion (Mass Law) Effect**
- **Special Salt Effect**

Kinetic Salt Effects: Ionic Strength

As the ionic concentration of a solvent system increases, the overall polarity of the medium increases. Increased solvent polarity favors ionization of neutral molecules.

Consider the hydrolysis of tert-butyl chloride shown below:

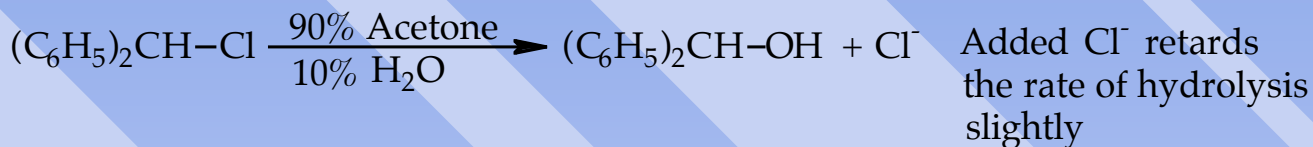
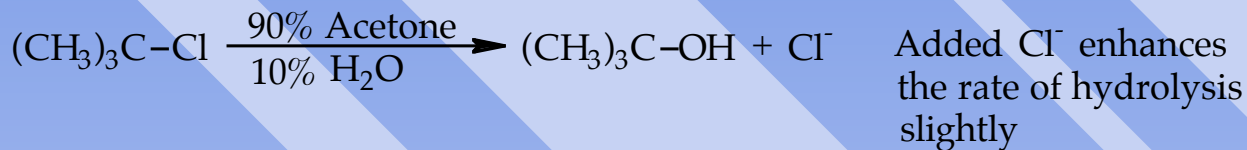


Observation: In both solvent systems, as the hydrolysis proceeds the reaction rate gradually increases. **The increase is more pronounced for the less aqueous medium**.

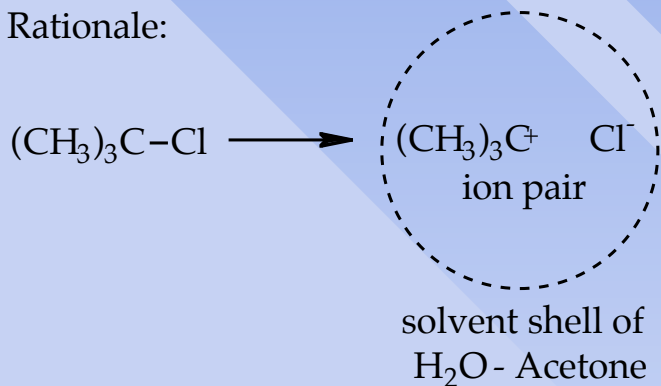
Rationale: As the hydrolysis reaction progresses, chloride ion concentration builds. The polarity of the medium increases favoring carbocation formation and subsequent attack by water to form product. The % increase in polarity is more keenly felt in the less aqueous (less polar) medium.

COMMON ION (MASS LAW) EFFECT

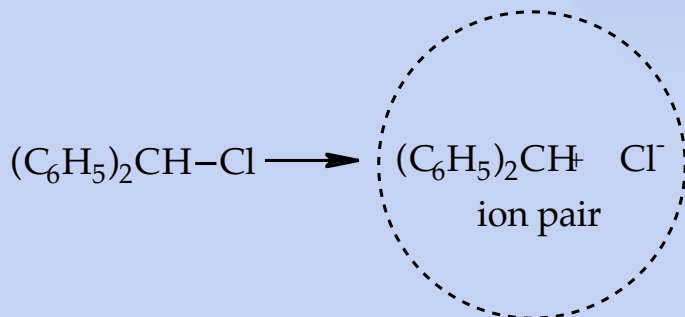
Consider the following observations:



Rationale:



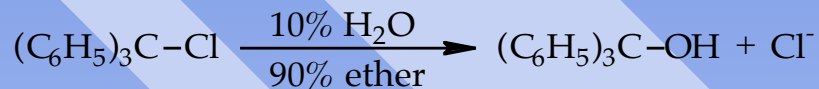
As soon as $(\text{CH}_3)_3\text{C}^+$ is formed, it reacts rapidly with the H_2O molecules in the solvent shell. Increasing the $[\text{Cl}^-]$ increases the polarity of the medium favoring $(\text{CH}_3)_3\text{C}^+$ formation.



$(\text{C}_6\text{H}_5)_2\text{CH}^+$ is a fairly stable (unreactive) carbocation. Although increasing the ionic strength of the medium favors its formation, $(\text{C}_6\text{H}_5)_2\text{CH}^+$ does not react immediately with H_2O from the solvent shell. During the lifetime of $(\text{C}_6\text{H}_5)_2\text{CH}^+$, the added Cl^- will favor return to reactant rather than conversion to product.

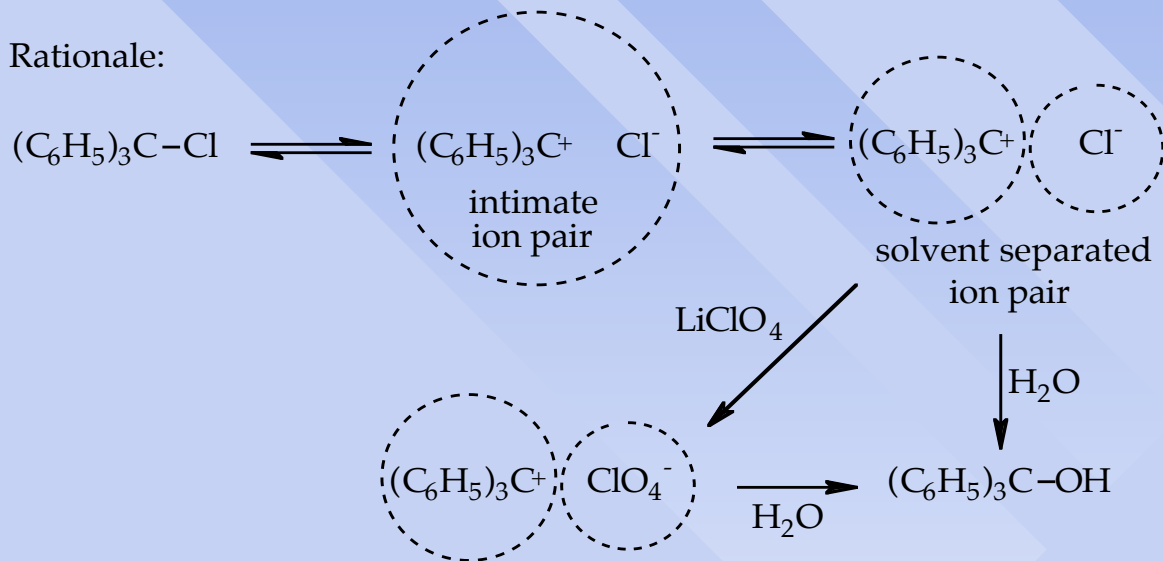
Special Salt Effect

Consider the following reactions:



Observation: In the presence of LiClO_4 , the rate of hydrolysis increases by a factor much larger than would be expected from an increase in ionic strength alone.

Rationale:



Perchlorate is essentially nonnucleophilic and is capable of displacing chloride from the solvent separated ion pair. By decreasing the likelihood of recombination of the intimate ion pair (regeneration of starting material), perchlorate permits more of the carbocation to form hydrolysis product per unit time.