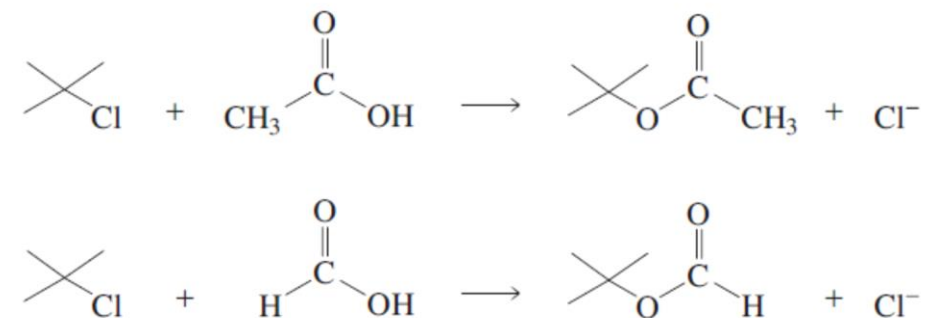
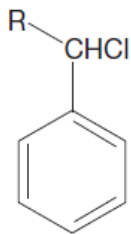


1. *tert*-Butyl chloride undergoes solvolysis in both acetic acid and formic acid. Solvolysis occurs 5000 times faster in one of the acids than in the other. In which solvent is solvolysis faster? Explain your answer. (Hint: The  $pK_a$  values of acetic acid and formic acid are 4.76 and 3.77, respectively).



Ans. The solvolysis will be faster in formic acid. Since its  $pK_a$  is lower, it will produce more amounts of carboxylate ion and proton through dissociation. This will lead to a higher ionic strength of the media and will accelerate the formation of the carbocation in formic acid.

2. Explain the relative rates of the following compounds in the  $S_N1$  reaction.

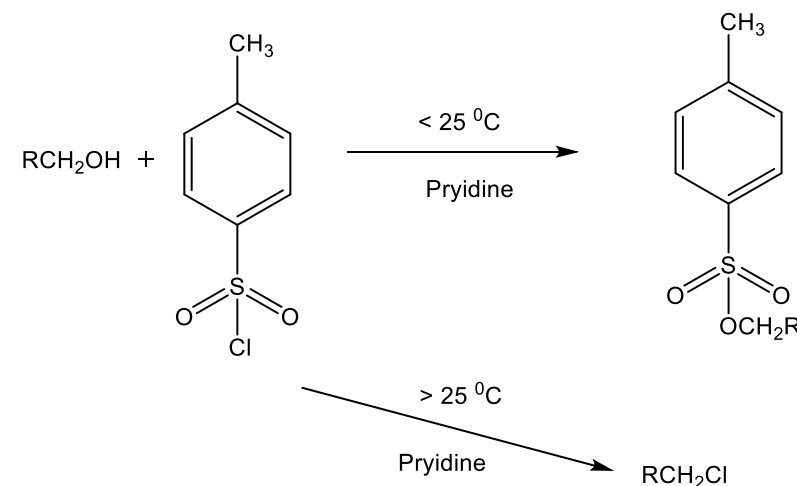
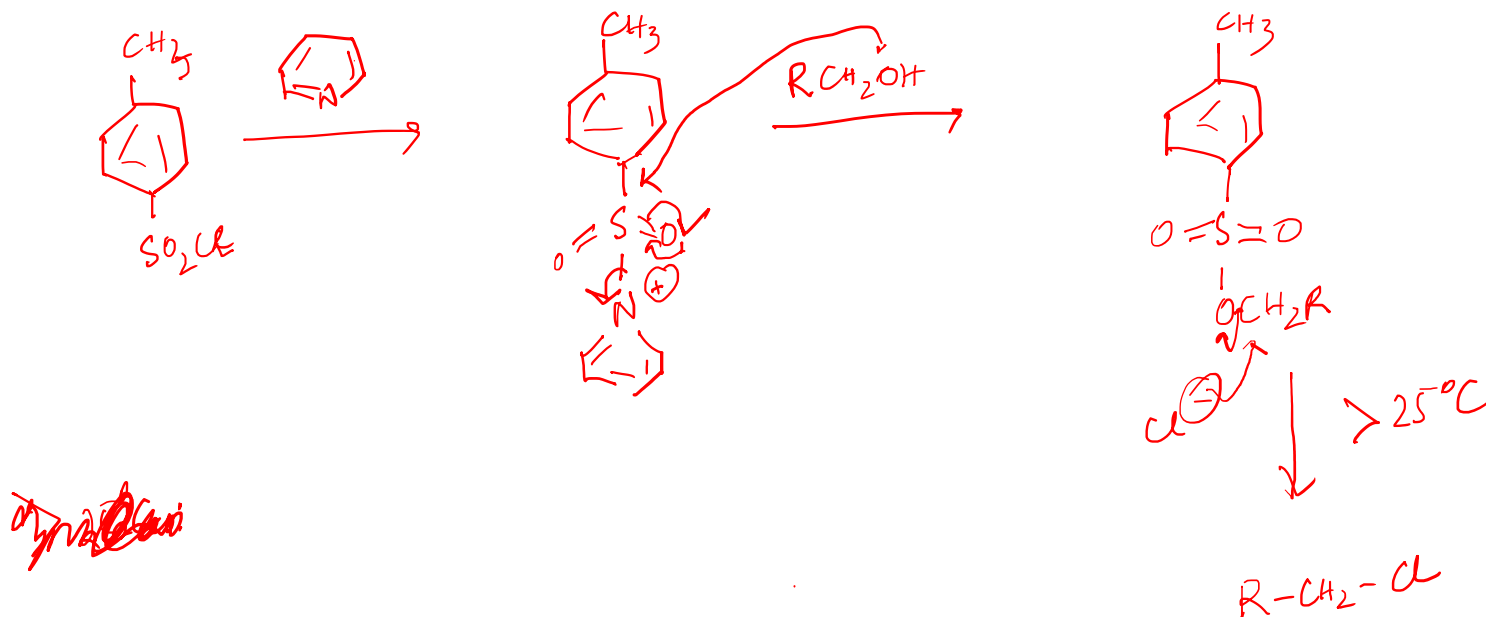


R	Relative Rate
$\text{CH}_3$	540
$\text{CH}_3\text{CH}_2$	125
$(\text{CH}_3)_2\text{CH}$	27
$(\text{CH}_3)_3\text{C}$	1

Ans. This is related to the stabilization of the carbocation through  $\sigma$ -conjugation. When  $\text{R} = \text{CH}_3$ , there are 3 C-H  $\sigma$ -bonds which can interact with the vacant p-orbital on the carbon bearing the positive charge. In the other three cases, this number is 2, 1 and 0, respectively. So, the carbocation with  $\text{R} = \text{CH}_3$  has the highest stability here through  $\sigma$ -conjugation. This also makes the activation energy of the formation of this carbocation lowest as the transition state in a  $S_N1$  reaction resembles the structure of the carbocation. Any stabilization in the carbocation would also lower the energy of the transition state and therefore the activation energy of its formation.

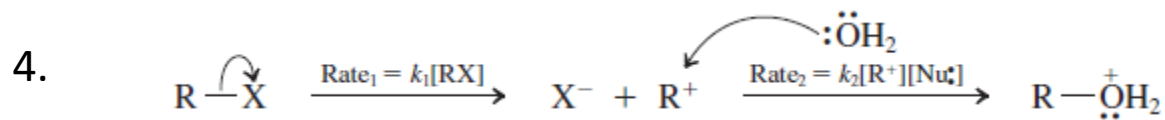
3. If the temperature is not kept below 25°C during the reaction of primary alcohols with p-toluenesulfonyl chloride in pyridine, it is sometimes observed that the isolated product is not the desired alkyl p-toluenesulfonate but is instead the corresponding alkyl chloride. Suggest a mechanistic explanation for this observation. What is the role of pyridine in this reaction? How do you explain the fact that the alkyl chloride is formed only above 25°C?

Ans. Pyridine acts as a nucleophilic catalyst, base and solvent for the reaction.

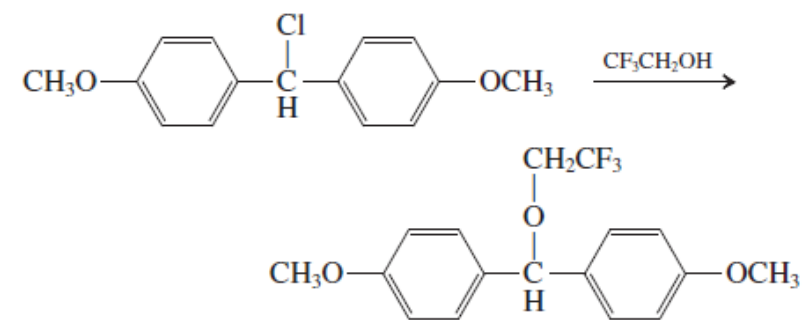


Pyridine reacts with the p-toluenesulfonyl chloride to produce a positively charged intermediate which reacts much faster with the alcohol and hence it acts as the nucleophilic catalyst.

The activation energy needed for the reaction between the  $\text{Cl}^-$  ion and the p-toluenesulfonate ester is provided by the thermal energy only above 25°C.



Loss of a proton gives the final product. Although there is considerable evidence for the intermediacy of a carbocation, it is not directly observed normally because its combination with a nucleophile is so rapid. Recently, examples of  $\text{S}_{\text{N}}1$  solvolyses have been found that give rise to very unusual observations. One example is the following:

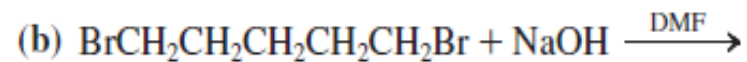
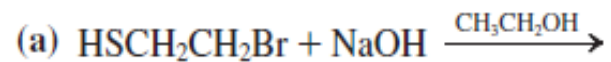


Upon mixing the colorless substrate and solvent, a reddish-orange color is observed immediately, signaling the formation of an intermediate carbocation. This color fades over a period of about a minute, and analysis of the solution reveals the presence of the final product in 100% yield. (a) There are two reasons for the build-up of a detectable concentration of carbocation in this case. Can you guess them? (hint: consider the carbocation as well as the solvent). (b) What can you say about the relative rates of the two steps (rate1 and rate2), and how do they compare to those in the usual  $\text{S}_{\text{N}}1$  reaction mechanism?

Ans. (a) The carbocation is very stable as it is stabilized through resonance (show the resonance structures). The solvent is a poor nucleophile due to the electron withdrawing effect of the  $-\text{CF}_3$  group.

(b) Rate1 will be faster than the usual  $\text{S}_{\text{N}}1$  reactions whereas rate2 will be slower.

5. Predict the products of the following reactions and explain mechanistically.



Excess

Ans.

