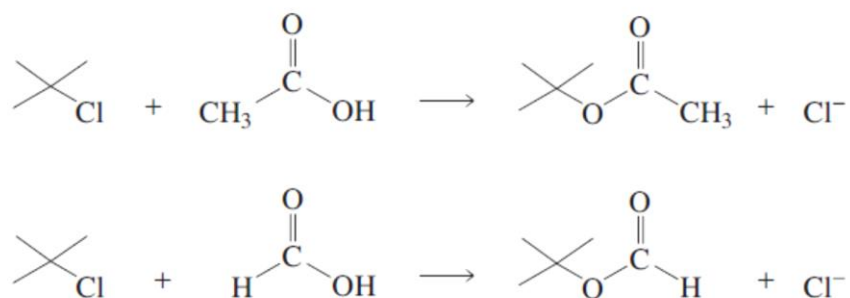
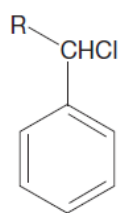


1. *tert*-Butyl chloride undergoes solvolysis in both acetic acid and formic acid.



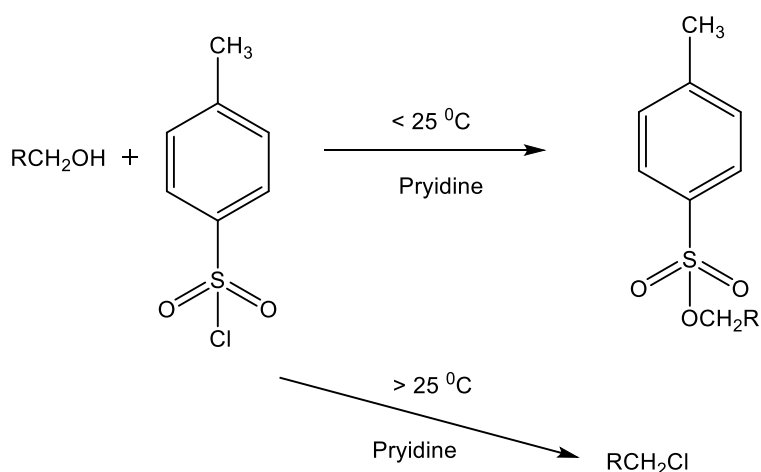
Solvolysis occurs 5000 times faster in one of the acids than in the other. In which solvent is solvolysis faster? Explain your answer. (Hint: The pK_a values of acetic acid and formic acid are 4.76 and 3.77, respectively).

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

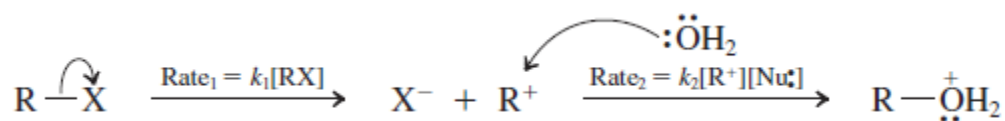


R	Relative Rate
CH ₃	540
CH ₃ CH ₂	125
(CH ₃) ₂ CH	27
(CH ₃) ₃ C	1

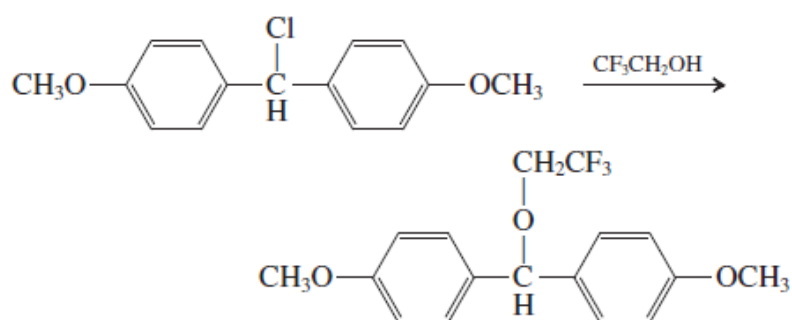
3. If the temperature is not kept below 25°C during the reaction of primary alcohols with *p*-toluenesulfonyl chloride in pyridine, it is sometimes observed that the isolated product is not the desired alkyl *p*-toluenesulfonate but is instead the corresponding alkyl chloride. Suggest a mechanistic explanation 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?



4. The S_N1 solvolysis reactions generally proceed according to the following scheme:



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 S_N1 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 S_N1 reaction mechanism?

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

