

Statistics:

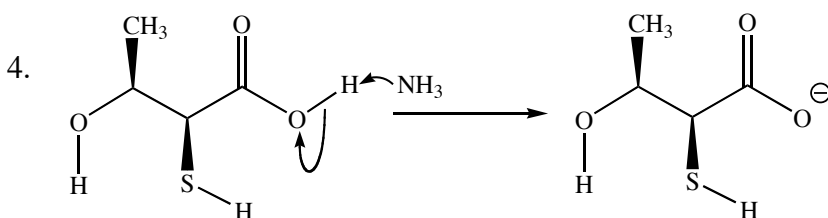
High score = 94 Average = 71.1 Low score = 08
 Standard Deviation = Irrelevant as it does not control grade distribution in this class.

A note about exam keys: The answers presented here are usually significantly longer than expected from a student taking the exam. An exam key serves not only to reveal what was expected, but to instruct you as well.

To see the final course grade cutoffs, consult the grading scale on the Chem 30A course web page.

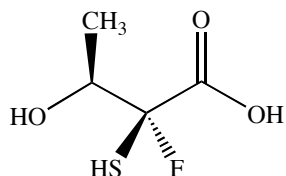
- ROH < RSH < RCO₂H
- Deprotonation of RCO₂H provides RCO₂⁻, which has resonance stabilization. RS⁻ and RO⁻ do not have resonance stabilization. Since resonance is the most influential factor when it comes to conjugate base stability, RCO₂⁻ is the most stable (weakest) conjugate base, so RCO₂H is the strongest acid. Comparing RSH and ROH, oxygen has a smaller atomic radius than sulfur, so oxygen cannot accommodate the negative charge as readily as sulfur. Therefore RS⁻ is a weaker base than RO⁻ and ROH is a weaker acid than RSH.

3. RCO₂H



Ammonia is the nucleophile and the carboxylic acid is the electrophile.

- $K_{eq} > 1$. Recall that an acid-base equilibrium favors the weakest acid/base pair. In this case ⁺H-base is the weaker acid (pK_a 10 > pK_a 5), so the equilibrium lies to the right.
- There are many solutions to this problem. Replacing a hydrogen atom with a fluorine atom makes the carboxylic acid group more acidic due to the inductive effect.

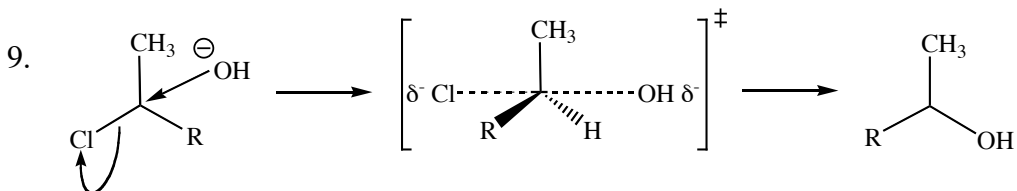


- (a) The name or structure of an important ion or molecule whose pK_a is -1.7 is **hydronium ion (H₃O⁺)**.

(b) Water is a poorer base than ammonia because **oxygen is more electronegative than nitrogen.**

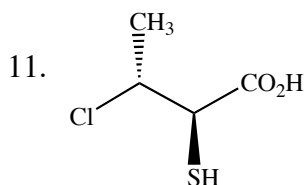
(c) Water is a poorer base than hydroxide ion because **water is neutral whereas hydroxide ion carries a formal negative charge.**

8. $\text{CF}_3\text{CH}_2\text{NH}_2$



10. (a) Along the reaction coordinate for any mechanism step, the transition state has the highest **potential energy** or ΔG .

(b) This is because **the transition state has one or more partial bonds.**



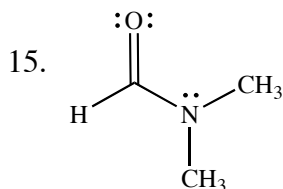
Recall that an $\text{S}_{\text{N}}2$ reaction occurs with inversion of stereochemistry at the carbon suffering substitution, but not at every stereocenter in the molecule.

12. Increased.

13. Reason #1: Triflate is a better leaving group than chloride because upon its departure it gains three significant resonance contributors, while chloride does not.

Reason #2: Triflate is a better leaving group than chloride because triflate enjoys an inductive stabilization of its negative charge by the CF_3 group. Chloride does not have this stabilization.

14. Decreases. (Water is a much poorer nucleophile than hydroxide ion.)

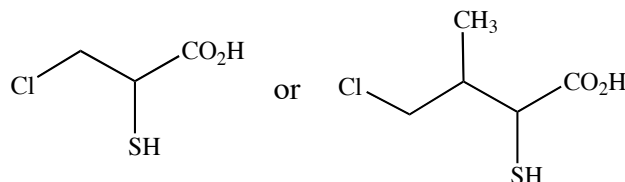


16. Increases.

17. Reason #1: DMF is more polar than ethanol.

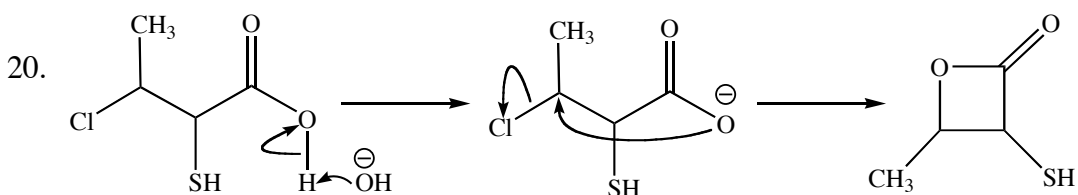
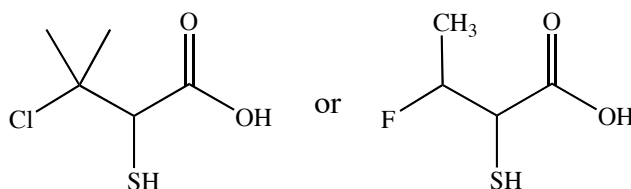
Reason #2: DMF is aprotic whereas ethanol is protic.

18. There are two solutions to this problem. For example you could delete a methyl group or install a methylene group (CH_2) between the Cl and CHCH_3 .



$\text{S}_{\text{N}}2$ rates: **Molecule A < 1° chloride**

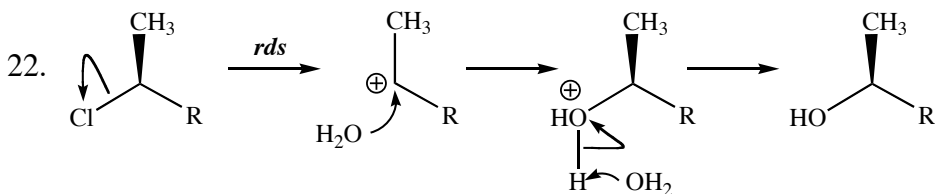
19. The $\text{S}_{\text{N}}2$ reaction will not occur if the carbon bearing the leaving group is tertiary (first structure) or if the leaving group is very poor (such as fluoride).



21. Factor #1: The product has a significant amount of ring strain.

Factor #2: A carboxylate ion (RCO_2^-) is not a very good nucleophile due to resonance delocalization of its negative charge.

Factor #3: Chloride ion is only a moderate leaving group.

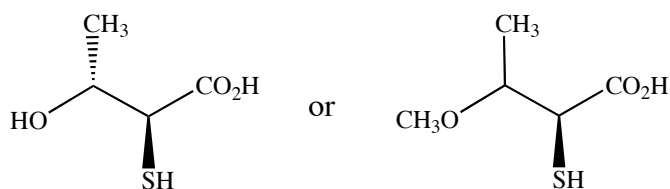


23. Reason #1: Water is a very poor nucleophile. It will undergo an $\text{S}_{\text{N}}2$ reaction only with the very best of leaving groups.

Reason #2: The product shown occurs from retention of stereochemistry at the carbon bearing the leaving group whereas an S_N2 reaction produces inversion of stereochemistry.

Chloride is a moderate leaving group, and is good enough for an S_N2 reaction. Methanol is protic, but a protic solvent does not prevent an S_N2 reaction. A secondary carbon does not provide enough steric hindrance to prevent an S_N2 reaction. Examine the text and Thinkbook for examples of S_N2 reactions in which chloride is the leaving group, or methanol is the solvent, or the carbon bearing the leaving group is secondary.

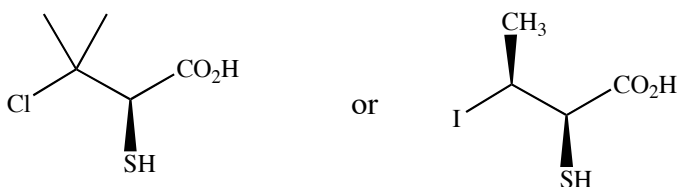
24. There are several possibilities, including the other alcohol diastereomer or products derived from methanol capture by the carbocation.



(Either diastereomer)

The thiol stereocenter is not inverted in this reaction. Remember that a carbocation can capture a nucleophile from either face, resulting in a mixture of stereoisomers at this carbon. Other stereocenters in the molecule are not altered. This leads to a mixture of stereoisomers, but not always a mixture of enantiomers. In this case the product is a mixture of diastereomers.

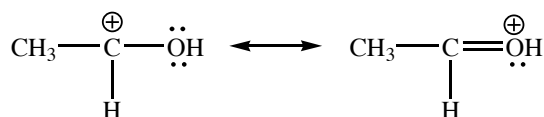
25. The S_N1 reaction is obviously faster if the carbocation is more stable or the leaving group is improved.



More substituted \rightarrow more stable carbocation

Better leaving group

26. If the carbocation has just two carbons it cannot be secondary, so the increased stability must be provided by resonance. Example:



27. $k = A_0 e^{-(\Delta G^\ddagger/RT)}$

28. A nucleophile shares an electron pair to form a new covalent bond. Higher electron density results in a stronger drive to share electrons. (Higher electron density causes more repulsion and gives the electrons greater potential energy.) This electron density can be stabilized by electrostatic attraction to neighboring positive charges. Stronger attraction provides greater the stabilization. Li^+ is smaller than Cs^+ and so its positive charge is more concentrated. The more concentrated positive charge provides more stabilization for the nucleophile's electron density. Thus LiOH is a poorer nucleophile than CsOH .