

Statistics: High score, average, and low score will be posted on the course web site after exam grading is complete. The exam is ready to be picked up when these numbers are posted.

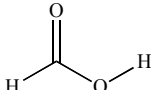
Some questions have more than one answer, even though only one answer may be listed here.

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

1. (a) $\text{CF}_3\text{CH}_2\text{SH}$ *Most favorable atomic radius and inductive effects.*

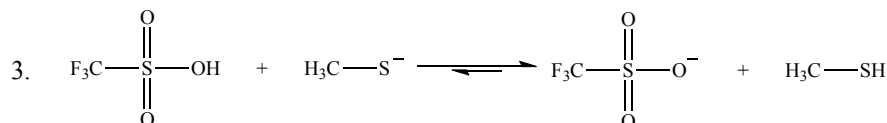
(b) CH_3OH *Most favorable electronegativity effect.*

(c) HOF *Most favorable inductive effect. Atomic radius does not apply because the proton is bonded to oxygen in each case.*

(d)  *Deprotonation of the carboxylic acids provide conjugate bases with more resonance stabilization than the corresponding acids. The second OH of HOCOOH increases electron density by resonance, making HOCO_2^- less stable than HCO_2^- .*

2. $\text{CF}_3\text{SO}_3\text{H}$ $\text{p}K_a$ -16; $\text{CH}_3\text{SO}_3\text{H}$ $\text{p}K_a$ -1.2; and CH_3SH $\text{p}K_a$ 10.7

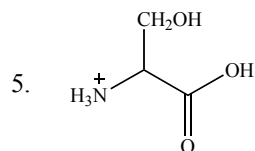
Resonance and inductive effects enhance the acidity of $\text{CF}_3\text{SO}_3\text{H}$ (i.e., the stability of its conjugate base.) $\text{CH}_3\text{SO}_3\text{H}$ has the resonance stabilization, but not the inductive stabilization. CH_3SH has neither resonance or inductive stabilization, so it is the weakest acid.



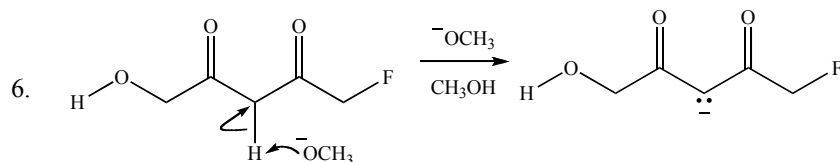
An acid-base equilibrium favors the weakest acid and weakest base. From question 2, CH_3SH is a weaker acid than $\text{CF}_3\text{SO}_3\text{H}$, so the equilibrium lies to the right.

4. More acidic molecule: Not possible.

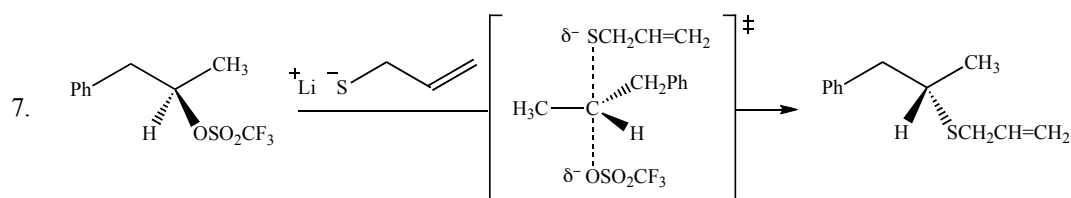
This is not possible because the more acidic molecule has a conjugate base with lower electron density. Methyl groups are electron donors, so their presence in the conjugate base increases electron density.



Because of its positive formal charge, $-\text{NH}_3^+$ is a stronger electron withdrawing group than $-\text{NH}_2$. Because of its negative formal charge, $-\text{CO}_2^-$ is a weaker electron withdrawing group than COOH . The $-\text{CO}_2^-$ group is better characterized as an electron donor group than an electron withdrawing group.

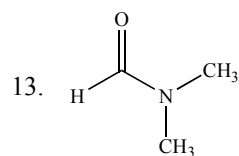
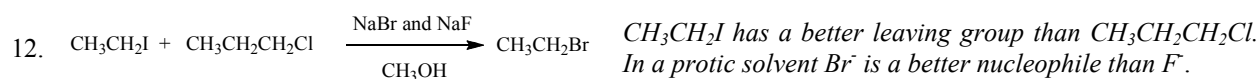


Deprotonation of the carbon between the carbonyls provides a conjugate base with three significant resonance contributors. All other conjugate base possibilities have less resonance stabilization.



Verify the structure of the transition state and product by using models.

8. 2° It is bonded to two additional carbon atoms. The hydrogen and oxygen do not count; only carbons count.
9. Acetone An S_N2 reaction between a negatively-charged nucleophile and neutral electrophile is fastest in an aprotic solvent of modest polarity. DMF, methanol, and ethanol are all more polar than acetone. Methanol and ethanol are protic.
10. (a) Reaction stops. CH_3O^- is not an S_N2 leaving group under any circumstances.
- (b) Reaction stops. An S_N2 reaction cannot proceed when the leaving group is bonded to a 3° carbon. This reaction will proceed via the S_N1 mechanism, but its S_N2 rate is zero.
- (c) About the same. The presence of the double bond does not have a significant impact on the electron density at the sulfur atom, so $^-SCH_2CH=CH_2$ and $^-SCH_2CH_2CH_3$ are of similar nucleophilicity.
11. Resonance: Enhances. Inductive effect: Enhances. Formal charge: Inhibits.

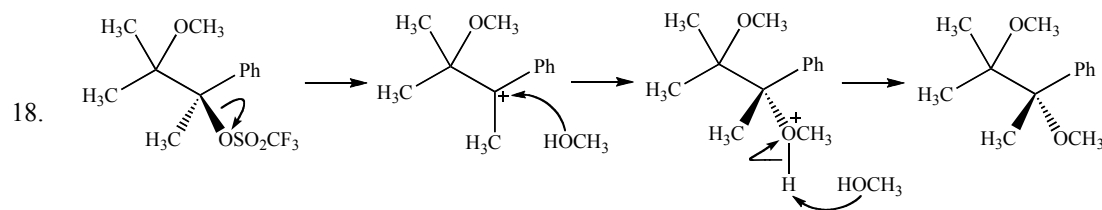


14. (a) $CF_3CO_2^-$ Leaving group ability enhanced by resonance and electron-withdrawing inductive effects.
- (b) $CH_3CH_2O^-$ Nucleophilicity enhanced by negative formal charge, and lack of resonance and electron-withdrawing inductive effects.
- (c) H_2O Has two highly polar bonds and no nonpolar bonds. The other choices all have a greater nonpolar/polar bond ratio.
15. (b) $(CH_3)_2S + CH_3I \xrightarrow[H_2O]{} (CH_3)_3S^+ I^-$

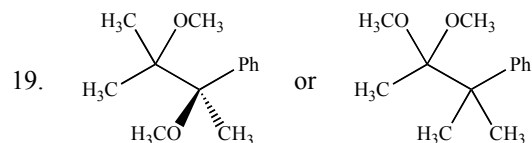
The fastest S_N2 reaction has the smallest energy difference between the reactants and transition state (i.e., the smallest E_{act} or ΔG^\ddagger). A polar solvent provides less stabilization for neutral reactants than it does for a transition state with partial charges.

16. (a) In an S_N2 reaction, the nucleophile attacks the electrophile from the backside of the carbon-leaving group bond because this is where the carbon-leaving group σ^* orbital is fattest.
- (b) In every S_N2 reaction, the transition state has higher energy than the reactants for that mechanism step because the transition state suffers more van der Waals (nonbonded or electron group) repulsion than the reactants.

17. The S_N2 reaction of 2-iodopropane has a lower reaction rate than the same S_N2 reaction of 1-iodopropane because 1-iodopropane has the lowest steric hindrance and therefore the lowest energy of activation.



CH_3OH is the base in the last step (instead of $CF_3SO_3^-$) because CH_3OH is a stronger base than $CF_3SO_3^-$. $CF_3SO_3^-$ is a case where resonance effects outweigh formal charge effects.



20. (a) Slower. $(CH_3)_3COH$ is less polar than CH_3OH .
- (b) Slower. Changing Ph to CH_3 removes resonance stabilization from the carbocation intermediate. ΔG^\ddagger for the carbon-leaving group bond ionization (an S_N1 reaction's rate-determining mechanism step) increases as the carbocation stability decreases.
- (c) About the same. Triflate anion ($CF_3SO_3^-$) and iodide anion are both excellent leaving groups. There is no compelling reason that triflate anion is a better or worse leaving group than iodide anion.
21. (a) An important factor that favors S_N1 and at the same time disfavors S_N2 is number of groups attached to the carbon bearing the leaving group. These groups enhance carbocation stability (matters for S_N1) but inhibit approach of the nucleophile (matters for S_N2). Methanol's poor nucleophilicity inhibits S_N2 , but does not make S_N1 any faster or any slower.
- (b) An important factor that favors S_N1 and at the same time does not disfavor S_N2 is triflate anion is a good leaving group.

Other answers may be possible.

22. Most stable: $^+CH_2NH_2$. Least stable: $^+CH_2CH_3$. Three of the carbocations have methyl carbons resonance stabilization, whereas $^+CH_2CH_3$ is 1° without resonance. Nitrogen is less electronegative than oxygen or fluorine, so nitrogen is a better resonance electron donor than oxygen or fluorine.

- 23.
- Faster ionization
Any molecule of formula $C_5H_{11}Br$ whose ionization gives a carbocation that is more stable than 2° . Only one structure is acceptable.
- Slower ionization
Any molecule of formula $C_5H_{11}Br$ whose ionization gives a carbocation that is less stable than 2° . Other structures may be acceptable.

24. (a) S_N1 The poor nucleophile disfavors S_N2 . Ionization of the carbon-iodine bond gives a carbocation that is secondary with resonance, stable enough for S_N1 .
- (b) S_N2 Moderate nucleophile, excellent leaving group, carbon bearing the leaving group is 1° , and the solvent is moderately polar and aprotic.
- (c) Neither. HO^- is not a leaving group in S_N2 or S_N1 reactions, except when protonated by strong acid, which is not present.