

POLAR PROTIC VS. POLAR APROTIC SOLVENTS

Answers document

Step-by-step discussions for each of these answers are available in the “Polar protic vs. polar aprotic solvents” video.

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Answers begin on next page.

Problem (a)

What is a polar molecule?

polar molecule: A polar molecule contains δ charges.¹

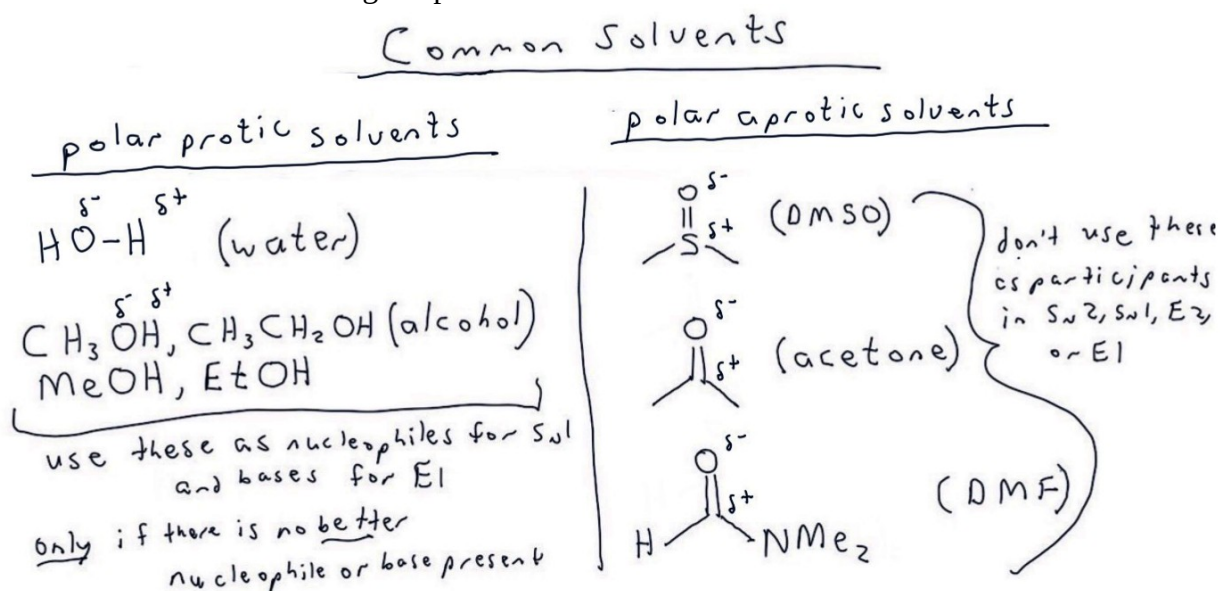
How does the electronegativity of hydrogen compare to the electronegativity of carbon?

The electronegativity of hydrogen is similar to the electronegativity of carbon. Notice that, unlike most other elements, you cannot judge the electronegativity of hydrogen by its position in the periodic table.

What does "more electronegative" mean?

If atom Y is more electronegative than atom Z, that means that atom Y "wants" electrons more than atom Z does.

Which of the following are polar solvents?



These are all polar solvents.

All of the solvents in the chart are polar solvents.

For example, consider acetone. Oxygen is to the right of carbon in the periodic table. This tells us that oxygen is more electronegative than carbon. This tells us that oxygen "wants" electrons more than carbon does. This tells us that the electrons in the covalent bonds between the oxygen and carbon will be drawn closer to the oxygen and further from the carbon. Since electrons have a negative charge, this will result in a δ^- charge on the oxygen and a δ^+ charge on the carbon.

For another example, consider H_2O (water). We have learned that hydrogen is similar to carbon in electronegativity. And we know that oxygen is more electronegative than carbon. This tells us that oxygen is also more electronegative than hydrogen. This tells us that oxygen "wants" electrons more than hydrogen does. This tells us that the electrons in the covalent bond between the oxygen and hydrogen will be drawn closer to the oxygen and further from the hydrogen. Since electrons have a negative charge, this will result in a δ^- charge on the oxygen and a δ^+ charge on the hydrogen.

¹ This is a simplified definition that is adequate for most ochem purposes.

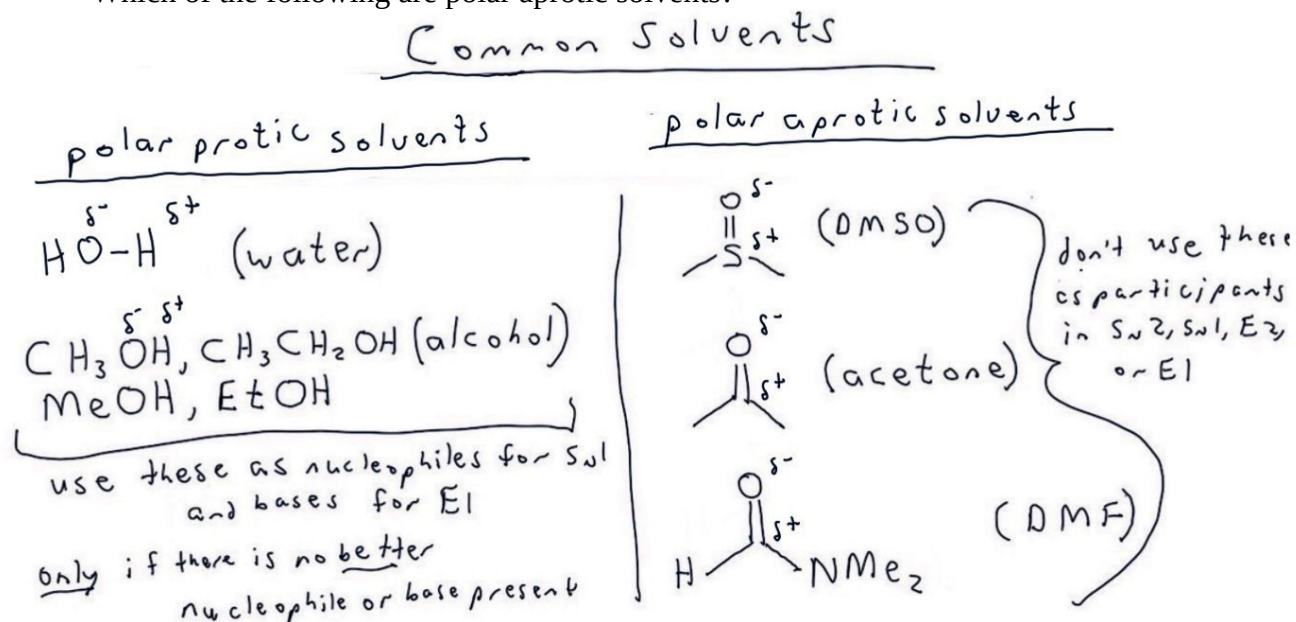
Problem (b)

How can you determine whether a solvent is "protic" or "aprotic"?

A protic solvent is a solvent that contains one or more O-H or N-H bonds.	An aprotic solvent is a solvent that does not contain any O-H or N-H bonds.
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Which of the following are polar protic solvents?

Which of the following are polar aprotic solvents?



These are all polar solvents.

Water (H_2O) has two O-H bonds, so water is a polar protic solventAn alcohol is a carbon chain connected to an OH group (such as CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$). An alcohol has an O-H bond, so an alcohol is a polar protic solvent.

DMSO, acetone, and DMF have no O-H or N-H bonds. Therefore, DMSO, acetone, and DMF are polar aprotic solvents.

(Notice that DMSO, acetone, and DMF all possess hydrogens, but the hydrogens are in C-H bonds, not in O-H or N-H bonds. A C-H bond does *not* qualify a molecule as a protic solvent.)

answers for problem (b) continue on next page

answer for Problem (b), continued

Is an S_N2 reaction faster in a polar protic solvent or in a polar aprotic solvent?

An S_N2 reaction is faster in a polar aprotic solvent, and slower in a polar protic solvent.

An explanation for this pattern will be given later in the video.

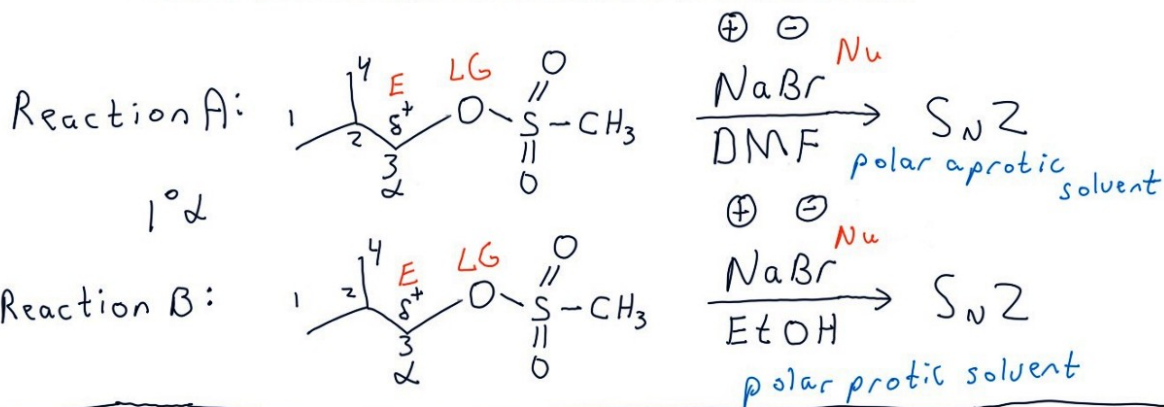
Is an S_N1 reaction faster in a polar protic solvent or in a polar aprotic solvent?

An S_N1 reaction is faster in a polar protic solvent, and slower in a polar aprotic solvent.

Answers continue on next page

Problem (c)

For the reactions below, which reaction will occur at the faster rate?



Reaction A will occur at the faster rate because it uses a polar aprotic solvent. The nucleophile is solvated more loosely in a polar aprotic solvent, and more tightly in a polar protic solvent. Therefore, the nucleophile can attack the α -carbon more easily in a polar aprotic solvent. Therefore, an S_N2 mechanism is faster in a polar aprotic solvent.

A protic solvent is a solvent that contains one or more O-H or N-H bonds.

An aprotic solvent is a solvent that does not contain any O-H or N-H bonds.

An S_N2 reaction is faster in a polar aprotic solvent, and slower in a polar protic solvent.

An S_N1 reaction is faster in a polar protic solvent, and slower in a polar aprotic solvent.

Notice that NaBr is a metal-nonmetal pairing, so NaBr represents an ionic bond. Draw in the formal charges for the ionic bond. Because the Br has a negative formal charge, the bromine will act as a nucleophile (electron donor).

Use the table to determine that the mechanism is S_N2 . Notice that if the mechanism were S_N1 , the answer would be reversed!

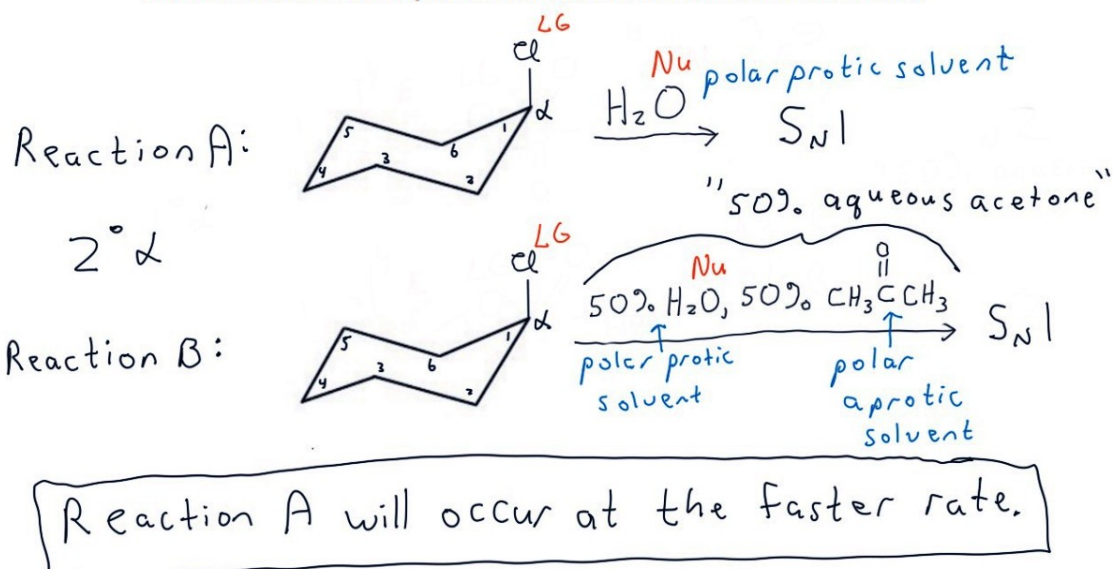
how to determine the mechanism for alkyl halides and alkyl sulfonates

	poor Nu / weak base O with no formal charge (water or alcohol)	good Nu / weak base Cl, <u>Br</u> , I, CN, S, N ₃ ⁻ or N, P, or S with no formal charge	good Nu / strong base O ⁻ , N ⁻
→ methyl α -carbon	no reaction	<u>S_N2</u>	S_N2
1° α -carbon			Exception: E2 with <i>t</i> -butoxide and 1° α -carbon
2° α -carbon	S_N1 major, E1 minor	S_N2	E2
3° α -carbon	S_N1 major, E1 minor	S_N1 major, E1 minor	E2

We know that EtOH is a polar protic solvent because of its OH bond. And we should have memorized that DMF is a polar aprotic solvent.

Problem (d)

For the reactions below, which reaction will occur at the faster rate?



A protic solvent is a solvent that contains one or more O-H or N-H bonds.

An aprotic solvent is a solvent that does not contain any O-H or N-H bonds.

An S_N2 reaction is faster in a polar aprotic solvent, and slower in a polar protic solvent.

An S_N1 reaction is faster in a polar protic solvent, and slower in a polar aprotic solvent.

Because there is no better nucleophile present, we use the water solvent (H_2O) as the nucleophile.

Use the table to determine that the mechanism is S_N1 . Notice that if the mechanism were S_N2 , the answer would be reversed!



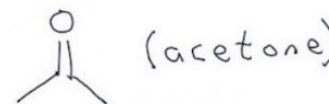
how to determine the mechanism for alkyl halides and alkyl sulfonates

	poor Nu / weak base O with no formal charge (water or alcohol)	good Nu / weak base Cl, Br, I, CN, S, N ₃ or N, P, or S with no formal charge	good Nu / strong base O ⁻ , N ⁻
methyl α-carbon	no reaction	S_N2	S_N2
1° α-carbon	no reaction	S_N2	Exception: E2 with <i>t</i> -butoxide and 1° α-carbon
2° α-carbon	S_N1 major, E1 minor	S_N2	E2
3° α-carbon	S_N1 major, E1 minor	S_N1 major, E1 minor	E2

We know that H_2O is a polar protic solvent because of its two O-H bonds.

We know that acetone is a polar aprotic solvent because it contains no O-H or N-H bonds.

Be aware that the combination of 50% water and 50% acetone may also be referred to by the description "50% aqueous acetone". ("Aqueous" = water.)



Since Reaction A has a 100% polar protic solvent, while Reaction B has a 50% polar aprotic solvent, Reaction A has the faster S_N1 reaction. **S_N1 is faster in a polar protic solvent.**

Problem (e)

What is the “big obstacle” to an S_N2 reaction?

The big obstacle to an S_N2 reaction is steric hindrance that blocks the nucleophile from attacking the α carbon.

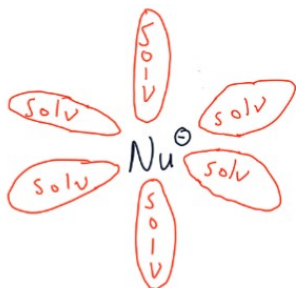
“Steric hindrance” means “things getting in each other’s way”.

Explain *why* an S_N2 reaction is faster in a polar aprotic solvent than in a polar protic solvent.

A polar protic solvent creates a tight solvation “shell” around the nucleophile. This shell of solvent molecules creates steric hindrance that hinders the nucleophile from attacking the α carbon. Therefore, S_N2 is slower in a polar protic solvent.

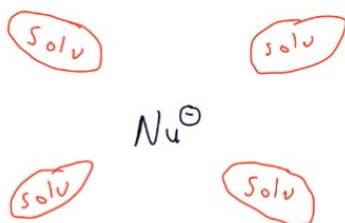
A polar aprotic solvent solvates the nucleophile more loosely than does a polar protic solvent. As a result, the solvent molecules in a polar aprotic solvent create less steric hindrance around the nucleophile, and so that it is easier for the nucleophile to attack the α carbon. Therefore, S_N2 is faster in a polar aprotic solvent.

**The big obstacle to an S_N2 reaction is:
steric hindrance that blocks the nucleophile
from joining the α -carbon.**



A polar protic solvent creates a tight solvation “shell” around the nucleophile.

polar protic solvents are worse for S_N2 because they create more steric hindrance around the nucleophile.

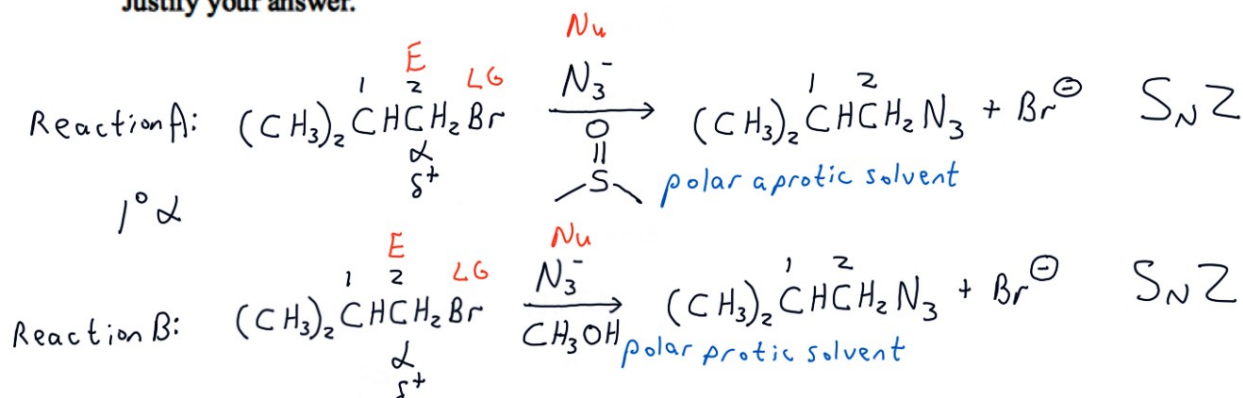


A polar aprotic solvent solvates the nucleophile more loosely.

polar aprotic solvents are better for S_N2 because they create less steric hindrance around the nucleophile.

Problem (f)

For the reactions below, which reaction will occur at the faster rate?
Justify your answer.



Reaction A will occur at the faster rate because it uses a polar aprotic solvent. The nucleophile is solvated more loosely in a polar aprotic solvent, and more tightly in a polar protic solvent. Therefore, the nucleophile can attack the α -carbon more easily in a polar aprotic solvent. Therefore, an $\text{S}_\text{N}2$ mechanism is faster in a polar aprotic solvent.

Because the N_3^- has a negative formal charge, the N_3^- will act as a nucleophile (electron donor).

Use the table to determine that the mechanism is $\text{S}_\text{N}2$. Notice that N_3^- is a special nucleophile that you can find in the middle column of the table. (Don't confuse N_3^- with an ordinary N^- , which appears in the right column of the table.)

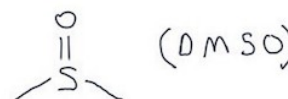
Make sure you determine the mechanism. If the mechanism were $\text{S}_\text{N}1$, the answer would be reversed!

how to determine the mechanism for alkyl halides and alkyl sulfonates

	poor Nu / weak base O with no formal charge (water or alcohol)	good Nu / weak base Cl, Br, I, CN^- , S_2N_2^- , or N, P, or S with no formal charge	good Nu / strong base O ⁻ , N ⁻
methyl α -carbon 1° α -carbon	no reaction	$\text{S}_\text{N}2$	$\text{S}_\text{N}2$ Exception: E2 with <i>t</i> -butoxide and 1° α -carbon
2° α -carbon	$\text{S}_\text{N}1$ major, E1 minor	$\text{S}_\text{N}2$	E2
3° α -carbon	$\text{S}_\text{N}1$ major, E1 minor	$\text{S}_\text{N}1$ major, E1 minor	E2

We know that CH_3OH is a polar protic solvent because of its O-H bond.

We know that DMSO is a polar aprotic solvent because it contains no O-H or N-H bonds.

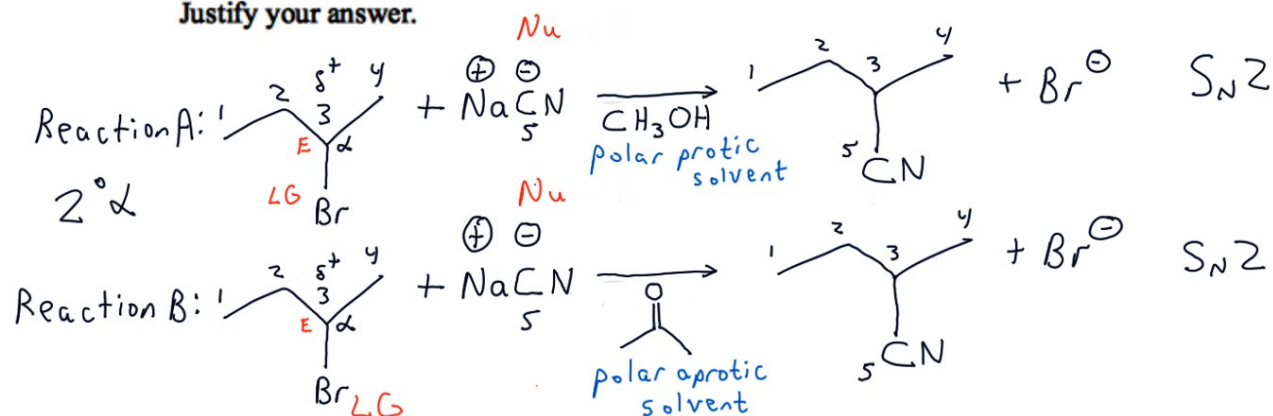


Be sure you *justify* your answer to this problem.

Problem (g)

For the reactions below, which reaction will occur at the faster rate?

Justify your answer.



Reaction B will occur at the faster rate because it uses a polar aprotic solvent. The nucleophile is solvated more loosely in a polar aprotic solvent, and more tightly in a polar protic solvent. Therefore, the nucleophile can attack the α -carbon more easily in a polar aprotic solvent. Therefore, an $\text{S}_{\text{N}}2$ mechanism is faster in a polar aprotic solvent.

\ Notice that NaCN is a metal-nonmetal pairing, so NaCN represents an ionic bond. Draw in the formal charges for the ionic bond. Because carbon 5 has a negative formal charge, carbon 5 will act as a nucleophile (electron donor).

Use the table to determine that the mechanism is $\text{S}_{\text{N}}2$. Notice that CN^- (cyanide ion) is a specific nucleophile that you can find in the middle column of the table.

Notice that if the mechanism were $\text{S}_{\text{N}}1$, the answer would be reversed!



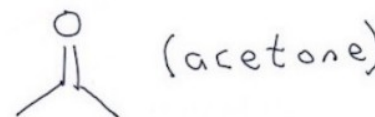
how to determine the mechanism for alkyl halides and alkyl sulfonates

	poor Nu / weak base O with no formal charge (water or alcohol)	good Nu / weak base Cl, Br, I, CN^- , S^- , N_3^- or N, P, or S with no formal charge	good Nu / strong base O ⁻ , N ⁻
methyl α -carbon	no reaction	$\text{S}_{\text{N}}2$	$\text{S}_{\text{N}}2$
1° α -carbon			Exception: E2 with <i>t</i> -butoxide and 1° α -carbon
2° α -carbon	$\text{S}_{\text{N}}1$ major, E1 minor	$\text{S}_{\text{N}}2$	E2
3° α -carbon	$\text{S}_{\text{N}}1$ major, E1 minor	$\text{S}_{\text{N}}1$ major, E1 minor	E2

In this table, the term " α -carbon" refers to the carbon attached to the leaving group.

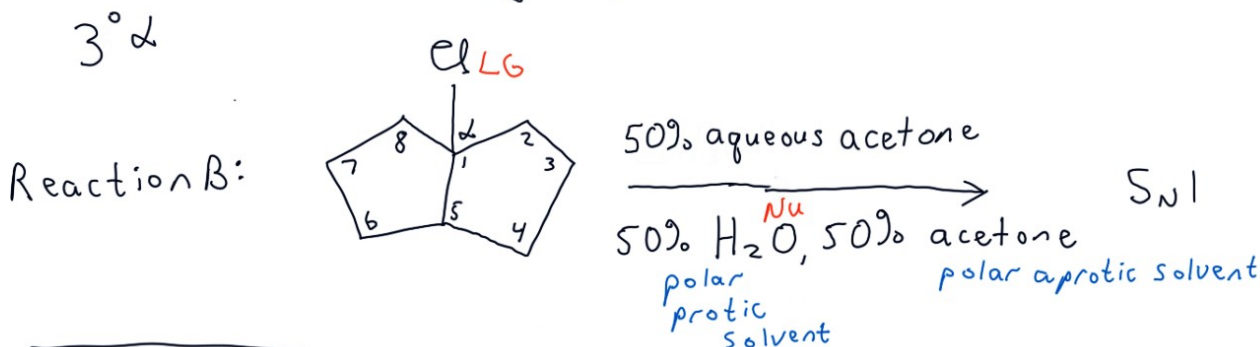
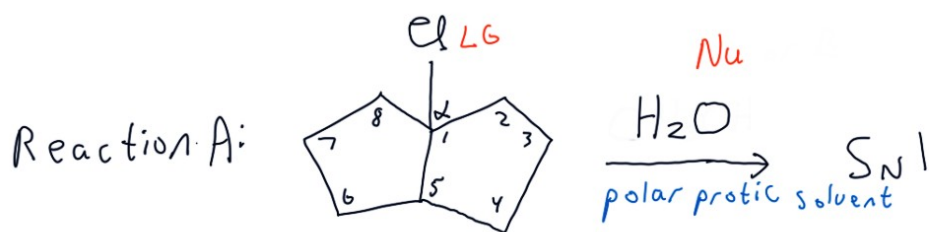
We know that CH_3OH is a polar protic solvent because of its O-H bond.

We know that acetone is a polar aprotic solvent because it contains no O-H or N-H bonds.



Problem (h)

For the reactions below, which reaction will occur at the faster rate?



Reaction A is faster.

 S_N1 mechanisms are faster in polar protic solvents.

“Aqueous acetone” means a solvent that consists of a mixture of 50% water (“aqueous”) and 50% acetone. Because there is no better nucleophile present, we use the water solvent (H_2O) as the nucleophile.

Use the table to determine that the mechanism is S_N1 . Notice that if the mechanism were S_N2 , the answer would be reversed!

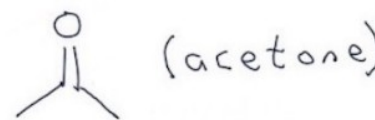


how to determine the mechanism for alkyl halides and alkyl sulfonates

	poor Nu / weak base O with no formal charge (water or alcohol)	good Nu / weak base Cl, Br, I, CN^- , S^- , N_3^- or N, P, or S with no formal charge	good Nu / strong base O ⁻ , N ⁻
methyl α -carbon	no reaction	S_N2	S_N2
1° α -carbon	no reaction	S_N2	Exception: E2 with <i>t</i> -butoxide and 1° α -carbon
2° α -carbon	S_N1 major, E1 minor	S_N2	E2
3° α -carbon	S_N1 major, E1 minor	S_N1 major, E1 minor	E2

We know that H_2O is a polar protic solvent because of its two O-H bonds.

We know that acetone is a polar aprotic solvent because it contains no O-H or N-H bonds.



Since Reaction A has a 100% polar protic solvent, while Reaction B has a 50% polar aprotic solvent, Reaction A has the faster S_N1 reaction.

S_N1 reactions are faster in a polar protic solvent.

Problem (i)

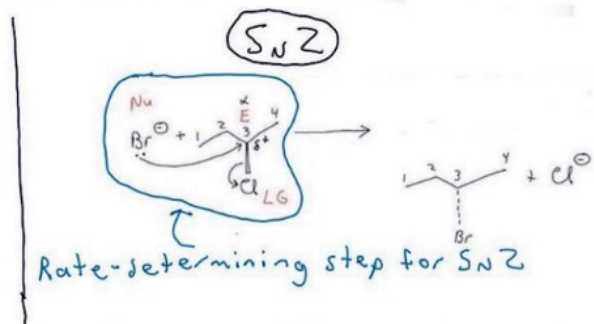
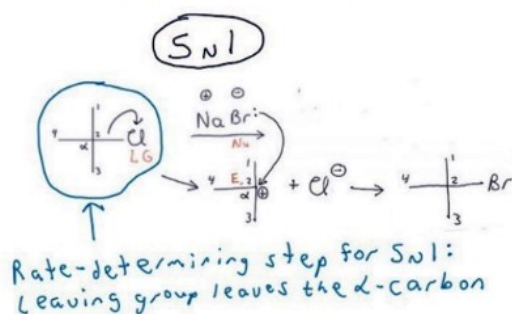
Steric hindrance is a big obstacle to an S_N2 mechanism, but steric hindrance is not a big obstacle to an S_N1 mechanism. Explain the difference.

FACTORS AFFECTING THE RATE FOR S_N1 AND S_N2 REACTIONS

rate-determining step: The slowest step in a reaction.

Anything that affects the rate determining step will affect the rate of a reaction.

Anything that does not affect the rate determining step will not affect the rate of the reaction.



The “rate-determining step” in a mechanism is the slowest step. Anything that affects the rate-determining step will affect the rate of the mechanism. Anything that does not affect the rate-determining step will not affect the rate of the mechanism.

An S_N2 mechanism consists of a single step, so that single step is the rate-determining step for S_N2 . In S_N2 , the nucleophile joins the α carbon during that rate-determining step. Therefore, steric hindrance that blocks the nucleophile from joining the α carbon is a big obstacle to an S_N2 mechanism.

An S_N1 mechanism consists of two steps. The slow, rate-determining step is the first step, formation of the carbocation. It is difficult to form the carbocation because the carbocation has a formal charge, and also because the carbocation has an incomplete octet.

In an S_N1 mechanism, the nucleophile does not attack the α carbon until Step Two. *Therefore, in a S_N1 mechanism, the nucleophile does not participate in the rate-determining step.* Therefore, steric hindrance that blocks the nucleophile is *not* a big obstacle to an S_N1 mechanism.

A polar protic solvent slows down an S_N2 mechanism, but a polar protic solvent does not slow down an S_N1 mechanism. Explain the difference.

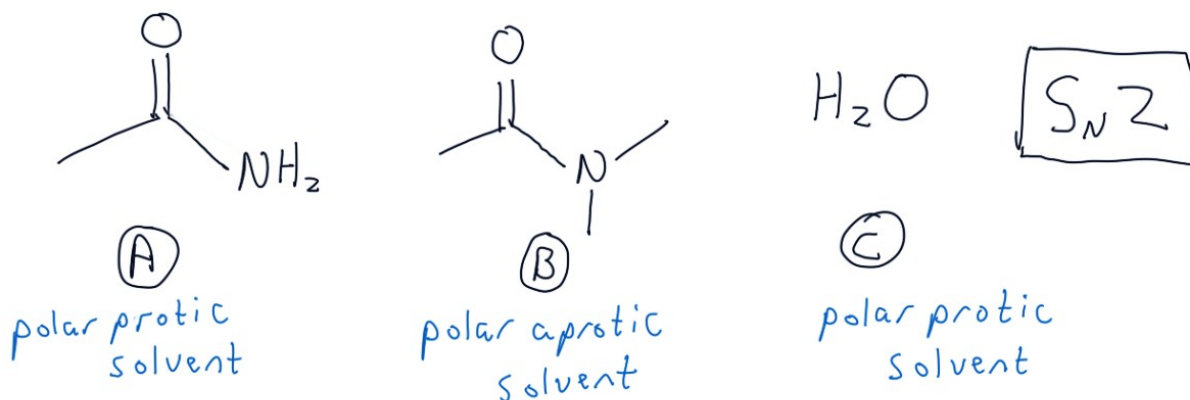
A polar protic solvent creates a tight solvation “shell” around the nucleophile. This shell of solvent molecules creates steric hindrance that hinders the nucleophile from attacking the α carbon.

Steric hindrance is a big obstacle to S_N2 , so the solvation shell created by a polar protic solvent slows down an S_N2 mechanism.

Steric hindrance is *not* a big obstacle to S_N1 , so the solvation shell created by a polar protic solvent does not slow down an S_N1 mechanism.

Notice that in this explanation, we have explained why a polar protic solvent does not slow down an S_N1 mechanism. However, we have not explained why a polar protic solvent *speeds up* an S_N1 mechanism. This explanation is more subtle and, in most introductory ochem courses, is not frequently tested, so we will not provide an explanation for why a polar protic solvent speeds up an S_N1 mechanism in this video. If you are interested, you can find an explanation in your textbook.

Problem (j)

Choose the best solvent for an S_N2 reaction.**Justify your answer.**

Solvent (B) is best for S_N2 because it is polar aprotic. A polar protic solvent (like (A) or (C)) would form a tight solvation shell around the nucleophile, hindering it from attacking the α carbon. A polar aprotic solvent will solvate the nucleophile more loosely.

Solvent A is protic because it contains two N-H bonds.

Solvent C (water) is protic because it contains two O-H bonds.

Solvent B is aprotic because it contains no O-H or N-H bonds.

(Notice that Solvents A and B are not included in the list of "common solvents" we saw earlier in the video. Nevertheless, we can still judge whether they are polar protic or polar aprotic, which is all we need to answer this question.)

For this problem, we know the mechanism is S_N2 because it is specified by the problem. *Pay close attention to the mechanism.* If the mechanism were S_N1 , solvent B would no longer be the best solvent!

A polar protic solvent solvates a nucleophile more tightly than does a polar aprotic solvent because a polar protic solvent can form hydrogen bonds to the nucleophile. The remaining answers in this document explore the importance of hydrogen bonding for this solvent effect.

You probably won't need to know the following material to get S_N2 solvent problems right on your exam. The following material is included mainly for those who are interested in deepening their understanding of hydrogen bonds, rather than for preparing for S_N2 solvent problems on exams. Hydrogen bonds are an important topic in many areas of organic chemistry and biochemistry.

Answers for problems about hydrogen bonding begin on the next page.

Problem (k)

What is a hydrogen bond?

A hydrogen bond is:

an attraction between a hydrogen with a large δ^+ and an atom with a negative formal charge or a δ^- .

Can polar protic solvents engage in hydrogen bonding?

A polar protic solvent has an O-H or N-H bond. Therefore, a polar protic solvent has a hydrogen with a large δ^+ charge. Therefore, yes, a polar protic solvent can engage in hydrogen bonding.

Can polar aprotic solvents engage in hydrogen bonding?

A polar aprotic solvent has no O-H or N-H bonds. Therefore, a polar aprotic solvent has no hydrogens with a large δ^+ charge. Therefore, no, a polar aprotic solvent cannot engage in hydrogen bonding.²

Why do polar protic solvents create a tight solvation shell around the nucleophile?

A protic solvent is a solvent that contains one or more O-H or N-H bonds.

So a protic solvent contains a hydrogen with a large δ^+ .

Therefore, a polar protic solvent can engage in hydrogen bonding.

Therefore, the polar protic solvent can engage in hydrogen bonding with the nucleophile.

Hydrogen bonding allows the polar protic solvent molecules to form a tight solvation shell around the nucleophile.

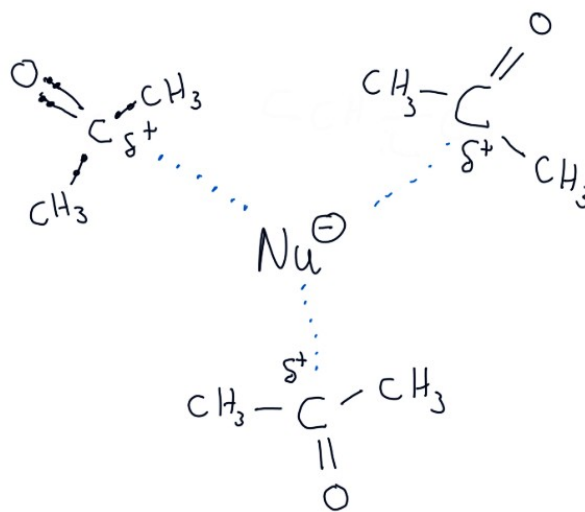
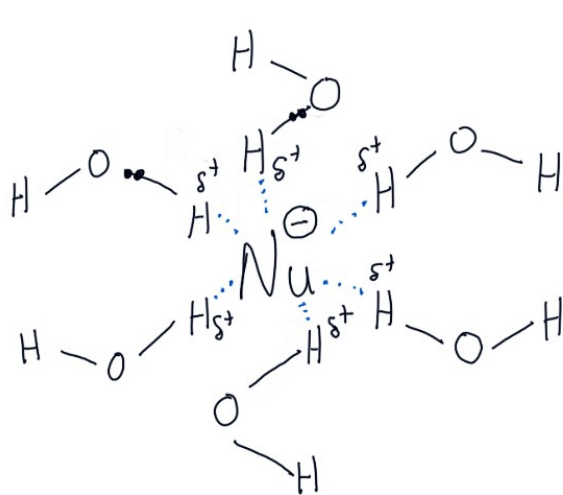
Why don't polar aprotic solvents create a tight solvation shell around the nucleophile?

An aprotic solvent is a solvent that does not contain any O-H or N-H bonds.

Therefore, an aprotic solvent is a solvent that does not contain any hydrogen with a large δ^+ .

Therefore, an aprotic solvent cannot engage in hydrogen bonding with the nucleophile.

Therefore, polar aprotic solvents solvate nucleophiles loosely.



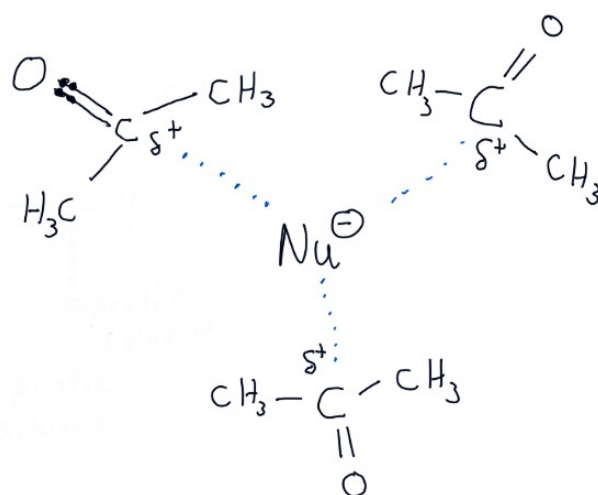
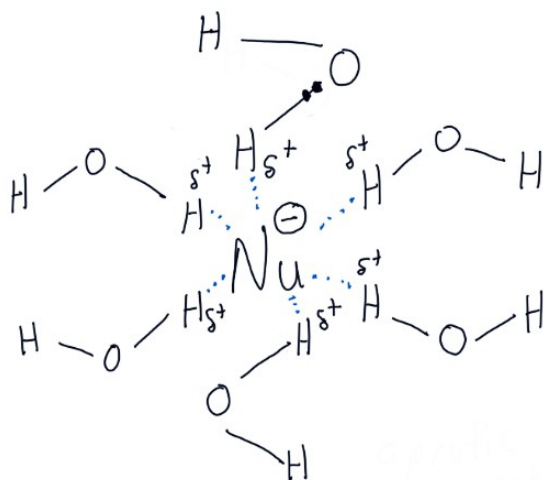
² Technically, a polar aprotic molecule cannot be a hydrogen bond *donor*. It can still be a hydrogen bond “acceptor”.

answer for Problem (k), continued

A hydrogen bond is:

an attraction between a hydrogen with a large δ^+ and an atom with a \ominus formal charge or a δ^- .

A protic solvent is a solvent that contains one or more O-H or N-H bonds.	An aprotic solvent is a solvent that does not contain any O-H or N-H bonds.
Therefore, a protic solvent contains a hydrogen with a large δ^+ .	Therefore, an aprotic solvent does not contain any hydrogen with a large δ^+ .
Therefore, a polar protic solvent can engage in hydrogen bonding.	Therefore, an aprotic solvent cannot engage in hydrogen bonding.
Therefore, polar protic solvents form tight solvation shells around nucleophiles.	Therefore, polar aprotic solvents solvate nucleophiles loosely.
A polar protic solvent decreases the rate of S_N2 by creating steric hindrance that blocks the nucleophile from joining the α carbon.	A polar aprotic solvent increases the rate of S_N2 , since it provides less steric hindrance to block the nucleophile from joining the α carbon.



In the left picture, the dots represent hydrogen bonds.

In the right picture, the dots represent “ion-dipole interactions”, which are looser than hydrogen bonds.

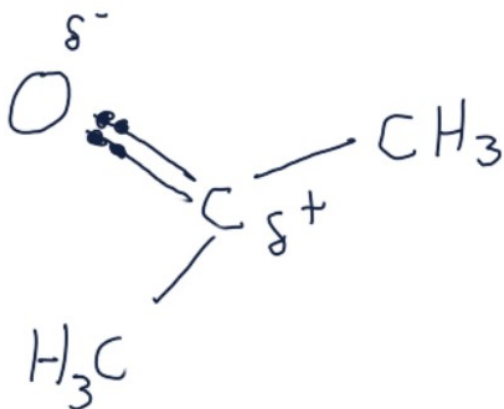
The solid lines are *not* hydrogen bonds. The solid lines are *covalent* bonds!

Covalent bonds are “intramolecular” (between two atoms in the same molecule.)

Hydrogen bonds and ion-dipole interactions are *intermolecular* attractions (between two different molecules or ions).

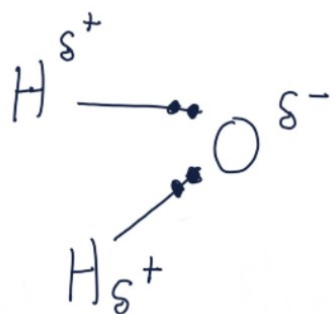
Problem (1)

Explain how the δ charges in acetone, shown below, are determined.



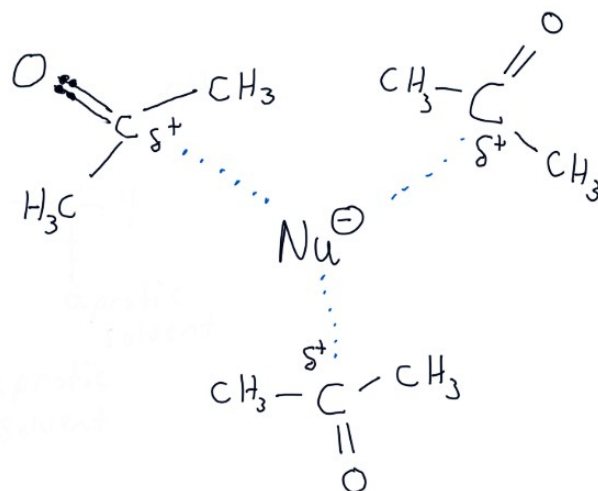
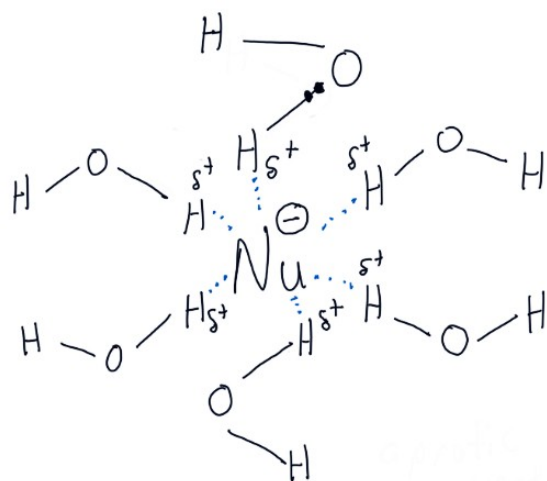
Oxygen is to the right of carbon in the periodic table. This tells us that oxygen is more electronegative than carbon. This tells us that oxygen “wants” electrons more than carbon does. This tells us that the electrons in the covalent bonds between the oxygen and carbon will be drawn closer to the oxygen and further from the carbon. Since electrons have a negative charge, this will result in a δ^- charge on the oxygen and a δ^+ charge on the carbon.

Explain how the δ charges in water, shown below, are determined.



We know that hydrogen is similar to carbon in electronegativity. (This is a fact we learned earlier in the video.) And we know that oxygen is more electronegative than carbon. This tells us that oxygen is also more electronegative than hydrogen. This tells us that oxygen “wants” electrons more than hydrogen does. This tells us that the electrons in the covalent bond between the oxygen and hydrogen will be drawn closer to the oxygen and further from the hydrogen. Since electrons have a negative charge, this will result in a δ^- charge on the oxygen and a δ^+ charge on the hydrogen.

Problem (m)



In the left picture, the dots represent hydrogen bonds.

In the right picture, the dots represent “ion-dipole interactions”, which are looser than hydrogen bonds.

Why are hydrogen bonds (in the left picture) a stronger, tight interaction than ion-dipole interactions (in the right picture)?

A hydrogen atom is unique because, unlike any other neutral atom, a neutral hydrogen consists of a *single* proton and a *single* electron.

Therefore, when the hydrogen’s single electron is partially drawn away from it in a polar covalent bond (as occurs in the O-H covalent bonds in water), all that is left is a single, almost “bare” proton *with no remaining cloud of nearby electrons*. (This is the reason that water is referred to as a “protic” solvent—the hydrogens act very similarly to bare protons.)

It is easy for this small, almost “bare” proton to get close to the Nu^- , forming a strong, tight interaction.

In contrast, consider the δ^+ carbon in acetone (right picture). A neutral carbon has 6 electrons and 6 electrons. So when 2 electrons are partially drawn away from the carbon in its polar covalent bonds to oxygen, the carbon still has 4 electrons left! Furthermore, there are two large clouds of electrons close to the δ^+ carbon, in its two attached methyl groups.

Because of its δ^+ charge, the carbon will be attracted to the Nu^- . However, all the electrons that are still close to the carbon will interfere with and weaken this attraction, preventing the carbon from forming the kind of strong, tight interaction with the Nu^- that would be formed in a “hydrogen bond”.