

5.6: NUCLEOPHILIC ADDITION OF WATER- HYDRATION

OBJECTIVES

After completing this section, you should be able to

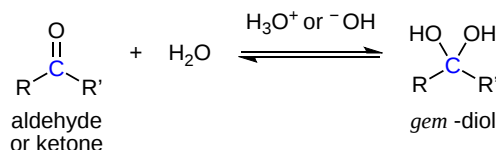
- write the step-wise mechanism for the base-catalyzed hydration of an aldehyde or ketone.
- write the step-wise mechanism for the acid-catalyzed hydration of an aldehyde or ketone.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- geminal (gem) diol

It has been demonstrated that water, in the presence of an acid or a base, adds rapidly to the carbonyl group of aldehydes and ketones establishing a reversible equilibrium with a **hydrate** (geminal-diol, *gem*-diol, or 1,1-diol). The term hydrate implies the addition of water. The word geminal or abbreviation gem comes from the Latin word for twin, *geminus*.

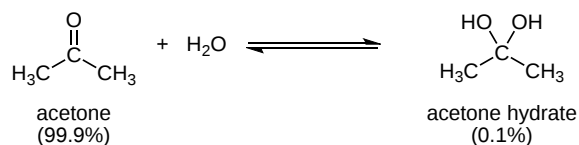
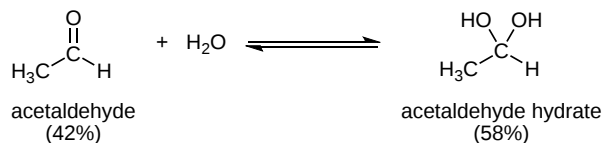
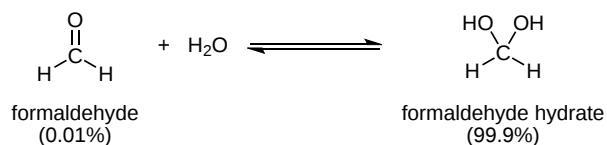


FACTORS AFFECTING THE HYDRATE EQUILIBRIUM

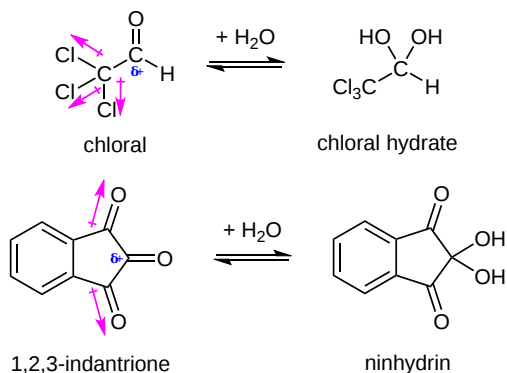
The equilibrium for hydrate formation depends both on steric and electrical factors of the carbonyl as discussed in the previous section. In most cases the resulting *gem*-diol is unstable relative to the reactants and cannot be isolated. Exceptions to this rule exist, one being formaldehyde where the small size of the hydrogen substituents relative to aldehydes and ketones favor hydrate formation. Thus, a solution of formaldehyde in water (formalin) is almost exclusively the hydrate, or polymers of the hydrate. The addition of electron donating alkyl groups stabilized the partial positive charge on the carbonyl carbon and decreases the amount of *gem*-diol product at equilibrium. Because of this ketones tend to form less than 1% of the hydrate at equilibrium.



Equilibrium Distribution of Common Aldehydes and Ketones with their Hydrate Forms

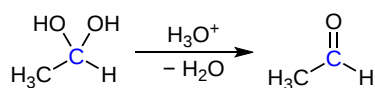


Likewise, the addition of strong electron-withdrawing groups destabilizes the carbonyl and tends to form stable hydrates. Two examples of this are chloral, and 1,2,3-indantrione. It should be noted that chloral hydrate is a sedative and has been added to alcoholic beverages to make a “knock-out” drink also called a Mickey Finn. Also, ninhydrin is commonly used by forensic investigators to reveal fingerprints.



REVERSIBILITY OF HYDRATE FORMATION

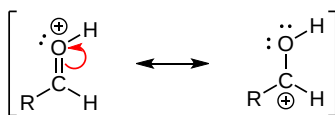
Isolation of hydrates is difficult because the reaction is reversible. Removal of water from the hydrate can cause the conversion of a gem-diol back to the corresponding carbonyl.



ACID OR BASE CATALYZED HYDRATE FORMATION

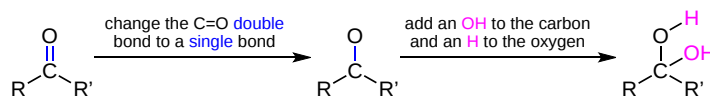
The nucleophilic addition of water to a carbonyl to form a hydrate is usually slow under neutral condition ($\text{pH} = 7$). The rate can be significantly increased through the addition of an acid or base as a catalyst.

The addition of an acid or base changes the mechanism and promote the nucleophilic addition of water to a carbonyl to form a hydrate. Basic conditions speed up the reaction because hydroxide is a better nucleophile than water. Acidic conditions speed up the reaction because the carbonyl becomes protonated. Protonation increases the polarity of the carbonyl bond which increase the partial positive charge on the carbon making it more electrophilic.

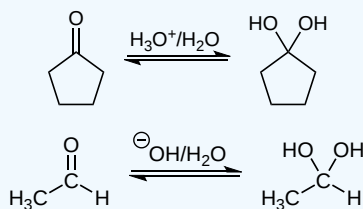


PREDICTING THE PRODUCT OF A HYDRATION

Overall, the $\text{C}=\text{O}$ of the carbonyl in the starting material is removed and replaced by two single bonds both of which are attached to the original carbonyl carbon. Both of these single bonds are attached to OH groups in the product.



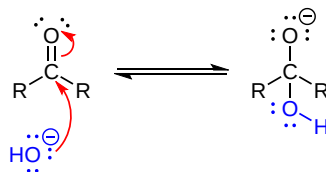
✓ EXAMPLE 5.6.1



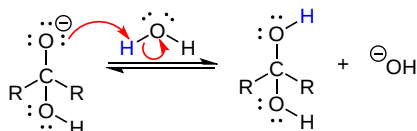
MECHANISM OF ACID OR BASE CATALYZED HYDRATE FORMATION

BASIC CONDITIONS

Step 1: Basic conditions means there is a significant amount of hydroxide present. Hydroxide is a better nucleophile than water which speeds up the reaction. The negatively charged hydroxide forms a single bond with the electrophilic carbonyl carbon. This pushes the two electrons of the pi bond onto the electronegative oxygen forming an alkoxide ion intermediate.

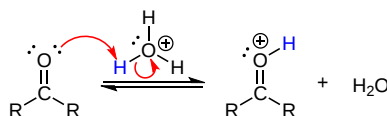


Step 2: Water acts as an acid and protonates the alkoxide ion to form a neutral hydrate while also regenerating hydroxide. The fact that hydroxide is not being used during the reaction is consistent with it acting as a catalyst.

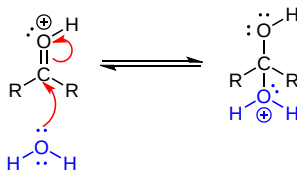


ACIDIC CONDITIONS

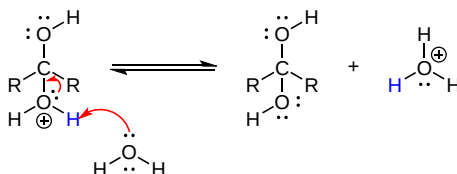
Step 1: Acidic conditions means there is a significant amount of hydronium present. Hydronium protonates the carbonyl oxygen thereby making the carbonyl carbon more electrophilic. After protonation the oxygen becomes positively charged.



Step 2: Under acidic conditions the most nucleophilic species is water. Water forms a single bond with the electrophilic carbon. This pushes the two electrons in the carbonyl pi bond onto the electronegative oxygen. The oxygen from the carbonyl becomes neutral while the oxygen from the water nucleophile becomes positively charged.

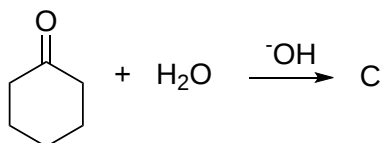
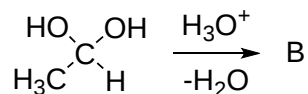
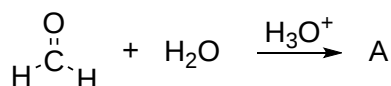


Step 3: Water acts as a base and deprotonates the intermediate to produce the neutrally charged hydrate while regenerating hydronium. The fact that hydronium is not being used during the reaction is consistent with it acting as a catalyst.

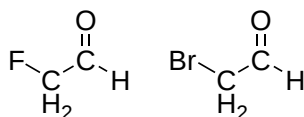


EXERCISES 5.6.1

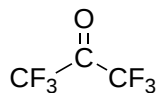
1) Draw the expected products of the following reactions.



2) Of the following pairs of molecules which would you expect to form a larger percentage of *gem*-diol at equilibrium? Please explain your answer.

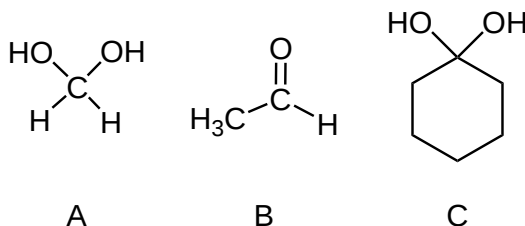


3) Would you expect the following molecule to form appreciable amount of *gem*-diol in water? Please explain your answer.



Answer

1)



2) The compound on the left would. Fluorine is more electronegative than bromine and would remove more electron density from the carbonyl carbon. This would destabilize the carbonyl allowing for more *gem*-diol to form.

3) Although ketones tend to not form *gem*-diols, this compound exists almost entirely in the *gem*-diol form when placed in water. Ketones tend to not form *gem*-diols because of the stabilizing effect of the electron donating alkyl group. However, in this case the electron donating effects of the alkyl group is dominated by the presence of six highly electronegative fluorines turning these into electron withdrawing groups.

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