You are already familiar with several types of isomeric relationships among organic molecules; constitutional isomers, conformational isomers, enantiomers, and diastereomers. Here is one more. Tautomers are two molecules with the same molecular formula but different connectivity - constitutional isomers, in other words - which can interconvert in a rapid equilibrium. The most common tautomeric relationship in organic chemistry is the keto-enol pair.

13.1A: Keto-enol tautomerization
13.1B: Imine-enamine tautomerization

Additional Resources

13.1A: Keto-enol tautomerization

When we draw a ketone or aldehyde using the Lewis structure convention, we show a double bond between the carbonyl carbon and the oxygen - this is known as the keto form. It turns out that ketones and aldehydes often exist in rapid equilibrium with a tautomeric form known as an enol.

\[
\begin{align*}
\text{keto form of acetone} & \quad \leftrightarrow \quad \text{enol form of acetone} \\
H_3C-C(\overset{\text{O}}{\text{C}})\text{CH}_3 & \quad \leftrightarrow \quad H_3C-C(\overset{\text{O}}{\text{H}})\text{CH}_2
\end{align*}
\]

The alpha-protons of carbonyls, as you recall, are somewhat acidic: the pK\textsubscript{a} of acetone, for example, is approximately 19. In the formation of an enol, a base abstracts an a-proton from a carbonyl compound, and that same proton (or a proton on a nearby acid group) is transferred to the carbonyl oxygen. The result is a new functional group that combines both alkene and alcohol characteristics - hence the term enol. The deprotonated form of an enol is an enolate.

\[
\begin{align*}
\text{keto} & \quad \leftrightarrow \quad \text{enolate} & \quad \leftrightarrow \quad \text{enol} \\
R-C(\overset{\text{O}}{\text{H}}) & \quad \leftrightarrow \quad R-C(\overset{\text{O}}{\text{B}^\text{\textsuperscript{\textbullet}}}) & \quad \leftrightarrow \quad R-C(\overset{\text{O}}{\text{H}})
\end{align*}
\]

As a general rule, the keto form of a carbonyl is lower in energy, and thus predominates at equilibrium. Acetone, for example, is present at >99% keto form at equilibrium.

Template:ExampleStart

Exercise 13.1: Draw all of the possible enol forms of the following aldehydes/ketones. There may be more than one possible enol form.

a. 3-pentanone
b. acetaldehyde (IUPAC name ethaldehyde)
c. cyclohexanone
d. 2-pentanone

**Exercise 13.2:** Draw three examples of aldehyde or ketone compounds for which there is no possible enol form.

**Solutions**

There are a few special cases where the enol form predominates at equilibrium: 2,4-pentane dione exists mostly in its enol form (76%), due to the extra stability of the conjugated double bonds that are present in the enol form, and due also to a favorable hydrogen bonding interaction.

![Enol to Keto Tautomerization](image)

Keto form (24%) \[\rightarrow\] Enol form (76%)

We saw a good example of an enol to keto tautomerization in the last step of the pyruvate kinase reaction (section 10.2F). The enol served as a leaving group in this phosphoryl transfer reaction, after which tautomerization occurred to form the ketone group of pyruvate.

![Pyruvate Kinase Reaction](image)

**13.1B: Imine-enamine tautomerization**

Another common tautomeric relationship in biological organic chemistry is the equilibrium between imines (also known as Schiff bases) and **enamines**, which are the nitrogen equivalents of enols.

![Imine-Enamine Tautomerization](image)

The degradation of serine, for example, involves an enamine to imine tautomerization step, followed by hydrolysis of the imine (section 11.6) to form pyruvate.
As we shall see in a later section, enamines are key intermediates in a very important type of carbon-carbon bond-forming reaction.

Additional Resources

Videos

keto-enol tautomerization

Keto-enol tautomerization video

Keto enol tautomer video