

# Summary Sheet 2: Enols and Enolates

Name	Structure	Example	pKa of H
aldehyde	<chem>R-C(=O)-H</chem>	<chem>H3C-C(=O)-H</chem>	17
ketone	<chem>R-C(=O)-R'</chem>	<chem>H3C-C(=O)-Me</chem>	20
ester	<chem>R-C(=O)-OR'</chem>	<chem>H3C-C(=O)-OMe</chem>	25
lactone (cyclic ester)	<chem>R-C(=O)-O-R'</chem>	<chem>H3C-C(=O)-O-CH2-CH2-</chem>	25
amide	<chem>R-C(=O)-NH2</chem>	<chem>H3C-C(=O)-NH2</chem>	30
lactam (cyclic amide)	<chem>R-C(=O)-NH-R'</chem>	<chem>H3C-C(=O)-NH-CH2-CH2-</chem>	30
carboxylic acid	<chem>R-C(=O)-OH</chem>	<chem>H3C-C(=O)-OH</chem>	4-5
acid chloride	<chem>R-C(=O)-Cl</chem>	<chem>H3C-C(=O)-Cl</chem>	1
anhydride	<chem>(R-C(=O))2-O</chem>	<chem>(H3C-C(=O))2-O</chem>	1
nitrile	<chem>R-C#N</chem>	<chem>Me-C#N</chem>	25

Alkyl = 1° alkyl  
 Aryl = 2° alkyl  
 Aryl = 3° alkyl

Note 1: The carboxylic acid is deprotonated first. Subsequent deprotonation of the  $\alpha$ -carbon would form a dianion, which has a high activation barrier due to charge repulsion. It can be done, but it requires a very strong base.

Note 2: It is difficult to measure the pKa of these species due to their reactivity.

Source: P. S. Bruck, "Organic Chemistry"

Note that some of these values differ slightly from textbook to textbook and instructor to instructor. However, there is universal agreement that for a given structure, pKa increases in the order aldehyde < ketone < ester < amide.

If you have a really different set of values I would appreciate it if you brought it to my attention.

For a comprehensive list of pKa values see:  
 Teyssie, Harvard.edu/cyfranczyk/pKa\_table.pdf  
 2) www.chem.wisc.edu/chem201/chem201/gktable/

### Structural Features of the Carbonyl Group

- Carbon, oxygen sp<sup>2</sup> hybridized
- O-C-O bond angle ~120°
- C=O bond strongly polarized toward oxygen
- Carbonyl carbon is partially positive (electrophilic)
- Lone pairs render oxygen weakly nucleophilic (will react with strong acids)



**Tautomerism:** a form of isomerism where a shift occurs by an atom through the movement of a proton and shifting of bonding electrons.

For acetone (R=CH<sub>3</sub>) the keto and enol is ~1000:1 at 20 °C. Main reason is the difference in bond strengths between the two species.

The enol tautomer is most significant for ketones and aldehydes. (They may also encounter it with acid chlorides in the mechanism of the Heck-Wittig-Catalytic reaction). Esters and amides are less acidic and exist almost exclusively as the keto form (e.g. >10<sup>21</sup>:1 keto:enol for ethyl acetate).

Acetone in D<sub>2</sub>O will slowly incorporate deuterium at the  $\alpha$ -carbon. The enol form is responsible for this behavior (the rate of ketone tautomerism is greatly increased by acid (see below right)).

Five factors that influence the relative proportion of tautomers:

- Aromaticity**  
  
 All phenols  $\rightleftharpoons$  Enolates
- Hydrogen bonding stabilizes the enol form**  
  
 24: 76 (at 20 °C)
- Strongly hydrogen bonding solvents can disrupt H-bonding**. The above equilibrium is 81:19 using water as solvent.
- Conjugation is stabilizing**  
  
 Preferred enol form
- As with alkenes, increasing substitution increases thermodynamic stability (assuming equal steric factors)

### Effects on acidity of alkyl groups

The carbonyl is an electron withdrawing system with leaving  $\pi^*$  orbitals. It stabilizes adjacent negative charge.



Why the huge difference in acidity? The lone pair is stabilized by donation into the carbonyl  $\pi^*$  system.



Question: How do you explain the relative acidity of the following bases?



Answer: The more electron-poor the carbonyl, the greater will be its ability to stabilize negative charge. Conversely, the greater the donating ability of a substituent on the carbonyl, the less it will be able to stabilize negative charge.

The anomeric stereoelectronic substitution that is a good proxy for the ability of a functional group to donate to a carbonyl:

NH2, O, C=C > OH > OR, NHR > CH3, R > Cl, Br, F > CO2R, CO2H, CF3, NO2

Substitution of the  $\alpha$ -carbon by a second carbonyl derivative makes the  $\alpha$ -proton even more acidic.



The rate of ketone interconversion is greatly enhanced by acid. Acid makes carbonyl more electrophilic, increasing acidity of  $\alpha$ -protons, facilitating formation of enol. This increases  $k_2$ .



Net result: Addition of acid speeds proton exchange between the keto and enol forms.

### Effect on reactivity of alkenes

Likewise, the presence of a carbonyl group activates alkenes toward nucleophilic attack.



The reactivity of the alkene toward nucleophilic attack is directly related to the stability of the enolate that forms.



Can predict the course of the reaction by pKa!

### Key Reaction: Enolate Formation



Important: the Enolate is a **NUCLEOPHILE**! Aliphatic, nucleophilic at both O and C, here we focus on the reactions at C.



The goal here is clarity and consistency. I would greatly appreciate feedback on any errors, omissions, or suggestions for improvements. Thanks!

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**Francis A. Carey, Richard J. Sundberg**



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