

Summary Sheet 2: Enols and Enolates

Name	Structure	Example	pK _a of H
aldehyde			17
ketone			20
ester			25
lactone (cyclic ester)			
amide			30
lactam (cyclic amide)			
carboxylic acid			Note 1
acid chloride			Note 2
anhydride			Note 3
nitrile			25

Note 1: The carboxylic acid is deprotonated first. Subsequent deprotonation of the α -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 pK_a of these species due to their reactivity.

*Source: P. S. Bruice, "Organic Chemistry"

Note that some of all these values differ slightly from textbook to textbook and instructor to instructor. However, there is universal agreement that for a given structure, pK_a 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 pK_a values see

*Tevens, Harvard edicyclotrains, pK_a table.pdf
 2) www.chem.wisc.edu/chem244/pKtable

Structural Features of the Carbonyl Group:

- Carbon, oxygen, sp² hybridized
- 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)

Key Concept: Tautomerism



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 (CH_3COCH_3) the keto and enol is ~1000:1 at 25 °C. Main reason is the difference in bond strengths between the two species.

The enol tautomer is most significant for ketones and aldehydes. (You may also encounter it with acid chlorides in the mechanism of the Heck-Wittig (Grob) reaction). Esters and amides are less acidic and exist almost exclusively as the keto form (e.g. $\sim 10^{-12}$ keto/enol for ethyl acetate).

Acetone in D_2O will slowly incorporate deuterium at the α -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:

1. Aromaticity



2. Hydrogen bonding stabilizes the enol form



3. Strongly hydrogen bonding solvents can disrupt this, however. The above equilibrium is 4:10 using water as solvent.

4. Conjugation is stabilizing



5. 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 low-lying π^* orbitals. It stabilizes adjacent negative charge.



Why the huge difference in acidity? The lone pair is stabilized by donation into the carbonyl π system.



Questions: How do you explain the relative acidity of the following series?



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 aromatic electrophilic substitution chart is a good proxy for the ability of a functional group to donate to a carbonyl.

NH_2 , O^- > OH > OR , NR_2 > CH_3 , R > O , In , F > COOH , CO_2R , CN

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



The rate of ketone interconversion is greatly enhanced by acid.

Acid makes carbonyl more electrophilic, increasing acidity of α -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 pK_a

Key Reaction: Enolate Formation

Enolate = deprotonated enol



Important: the Enolate is a **NUCLEOPHILE**

Electrophilic nucleophilicity at both O and C, here we focus on the reactions at C

Two key examples:



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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