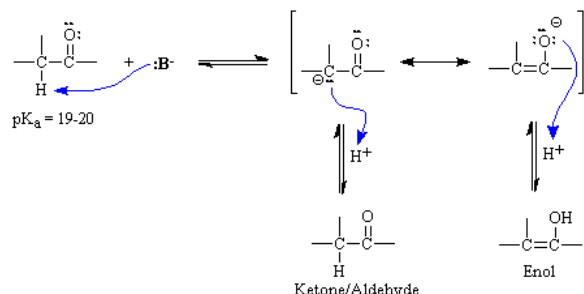


23.1: RELATIVE ACIDITY OF ALPHA-HYDROGENS

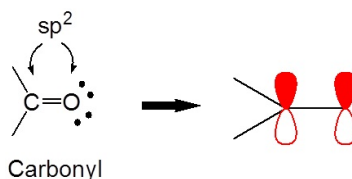
ACIDITY OF ALPHA HYDROGENS

Alkyl hydrogen atoms bonded to a carbon atom in a α (alpha) position relative to a carbonyl group display unusual acidity. While the pK_a values for alkyl C-H bonds is typically on the order of 40-50, pK_a values for these alpha hydrogens is more on the order of 19-20. This can most easily be explained by resonance stabilization of the product carbanion, as illustrated in the diagram below.

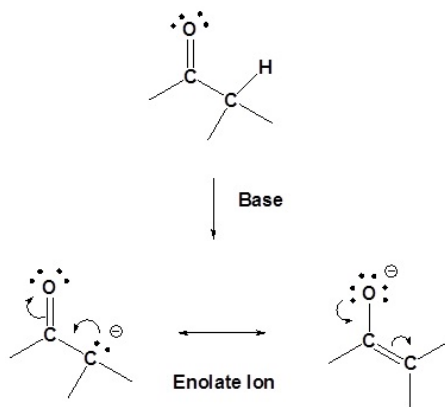


In the presence of a proton source, the product can either revert back into the starting ketone or aldehyde or can form a new product, the enol. The equilibrium reaction between the ketone or aldehyde and the enol form is commonly referred to as "keto-enol tautomerism". The ketone or aldehyde is generally strongly favored in this reaction.

Because carbonyl groups are sp^2 hybridized the carbon and oxygen both have unhybridized p orbitals which can overlap to form the $C=O$ π bond.



The presence of these overlapping p orbitals gives α hydrogens (Hydrogens on carbons adjacent to carbonyls) special properties. In particular, α hydrogens are weakly acidic because the conjugate base, called an enolate, is stabilized through conjugation with the π orbitals of the carbonyl. The effect of the carbonyl is seen when comparing the pK_a for the α hydrogens of aldehydes ($\sim 16-18$), ketones ($\sim 19-21$), and esters ($\sim 23-25$) to the pK_a of an alkane (~ 50).



Of the two resonance structures of the enolate ion the one which places the negative charge on the oxygen is the most stable. This is because the negative charge will be better stabilized by the greater electronegativity of the oxygen.

RELATIVE ACIDITY OF ALPHA HYDROGENS

The acidity of alpha hydrogens varies by carbonyl functional group as shown in the table below. Evaluating the stability of the conjugate bases can explain the differences in the relative acidity of the alpha hydrogens.

Compound	pKa
$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array}$	50
$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{C}-\text{C}-\text{OR} \\ \\ \text{H} \end{array}$	25
$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{C}-\text{C}-\text{R} \\ \\ \text{H} \end{array}$	20
$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{C}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	17
$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{HC}-\text{CH}-\text{C}-\text{OR} \\ \\ \text{H} \end{array}$	11
$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{HC}-\text{CH}-\text{C}-\text{R} \\ \\ \text{H} \end{array}$	9
$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{HC}-\text{CH}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	6

The ionizable proton for each compound is bonded to an sp^3 hybridized carbon.

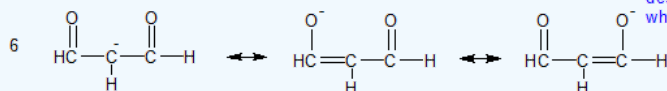
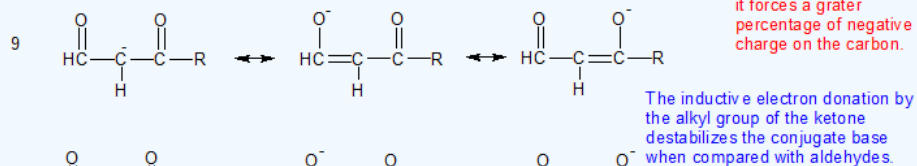
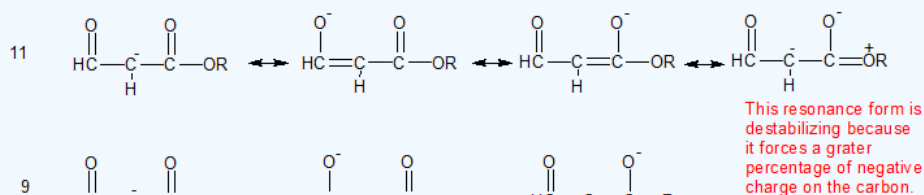
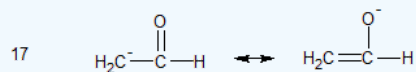
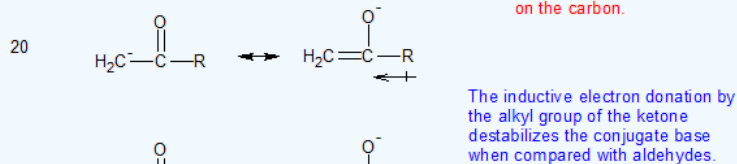
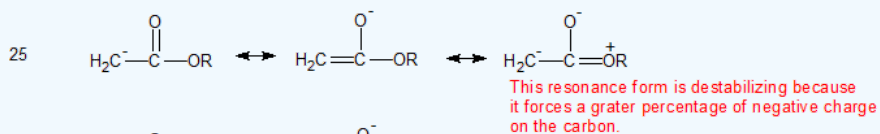
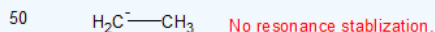
Exercise

1. Draw the bond line structure for each compound in the table above including all relevant resonance forms to explain the relative acidity.

Answer

1.

pKa



CONTRIBUTORS AND ATTRIBUTIONS

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