Acids And Bases

A. Introduction

B. Log Scales To Measure Proton Dissociation From Organic Molecules

Equilibria That Generate Protons

hats not worn at any moment is a *constant*, because an equilibrium

of hats worn at equilibrium in *different* games will be *variable*; therefore, it *is not* a good parameter

the *ratio* of *people wearing hats* to *people not wearing hats will not* change significantly

This *is* effectively the same as the statement:

protons in acid base equilibria *may* be represented as:

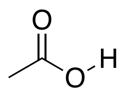
to generate protons for *all* organic

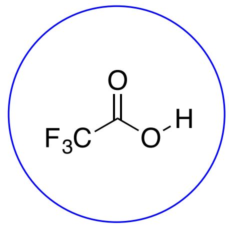
Weak acids dissociate to give a *small* fraction

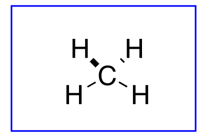
compound is a *strong* acid and the equilibrium constant is *high*.

methane is therefore a *weak* acid.

therefore a significantly *stronger* acid than methane.

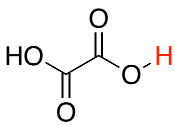
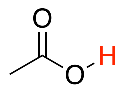
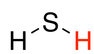
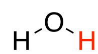
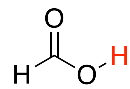
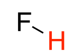






the number of moles of CH_3^- *does* equal the concentration of protons

10^{60} 10^{6} 10 1 10^{-6} 10^{-60}

					
$K_a = 5.4 \times 10^{-2}$	1.8×10^{-5}	1.1×10^{-7}	1.0×10^{-14}	2.4×10^{-4}	6.6×10^{-4}
1	4	5	6	3	2

with a K_a of 1 would be a *strong* acid.

and $[H^+] = \dfrac{K_a\ [CH_3COSEt]}{[^-CH_2COSEt]}$

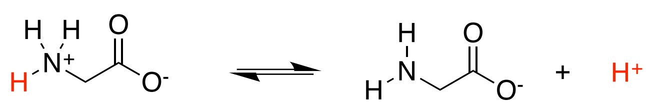
____

and $[H^+] = \dfrac{K_a\ [CH_3CO_2H]}{[CH_3CO_2^-]}$

____

and $[H^+] = \dfrac{K_a\ [CHCH]}{[CHC^-]}$

____



and $[H^+] = \dfrac{K_a\ [^+NH_3CH_2CO_2^-]}{[NH_2CH_2CO_2^-]}$

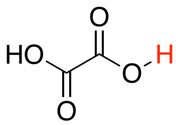
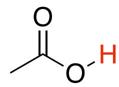
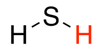
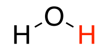
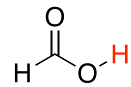
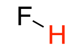
____

and $[H^+] = \dfrac{K_a\ [CH_3COCH_3]}{[CH_3COCH_2^-]}$

____

Simplifying The Scale: pKa

condenses

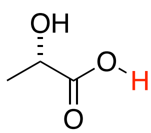







$K_a = 5.4 \times 10^{-2}$	1.8×10^{-5}	1.1×10^{-7}	1.0×10^{-14}	2.4×10^{-4}	6.6×10^{-4}
$\log K_a = -1.27$	$\log K_a = -4.74$	$\log K_a = -6.95$	$\log K_a = -14$	$\log K_a = -3.74$	$\log K_a = -3.18$
$-\log K_a = 1.27$	$-\log K_a = 4.74$	$-\log K_a = 6.95$	$-\log K_a = 14$	$-\log K_a = 3.74$	$-\log K_a = 3.18$

diagram above the values for $-\log K_a$, *ie* the *pK_a* value.

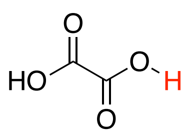
have K_a values less than one, meaning *only a small amount* of the compound
using negative logs of K_a values is they are *positive* for most organic compounds.

Strong acids have *larger* K_a values than weak acids, *less* $-\log K_a$ values, and *smaller* pK_a values.



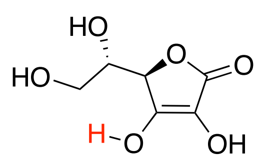
lactic acid
$pK_a = 3.86$

2



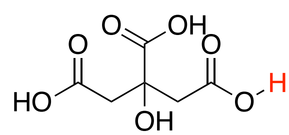
oxalic acid
4.19

4



ascorbic acid
4.10

3



citric acid
3.08

1

one pK_a unit means that it is *10* times easier

10 pK_a units means that it is *10,000,000,000* times easier

NH_4^+	NH_3	H_3O^+	H_2O
ammonium	*ammonia*	*hydroxonium*	*water*
pK_a = 9.2	*38*	*-1.7*	*14.0*
2	4	1	3

it is about 10^{29} times *more* likely that an ammonium ion

it is about 10^{17} times *less* likely that water will dissociate

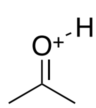
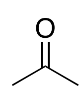
C. Acid-Base Equilibria

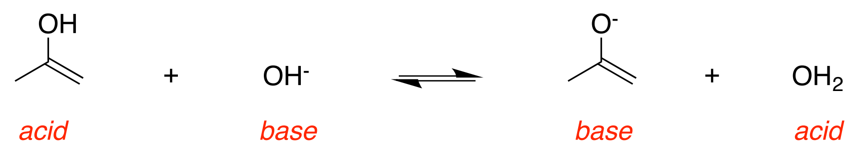
following equilibrium favors the *starting materials*

NH_4^+	+	H_2O	$\rightleftharpoons$	NH_3	+	H_3O^+
acid		*base*		*base*		*acid*

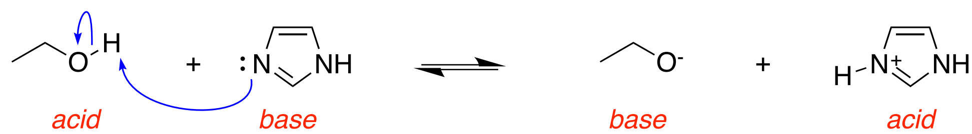
favor the side with the *weakest* acid because

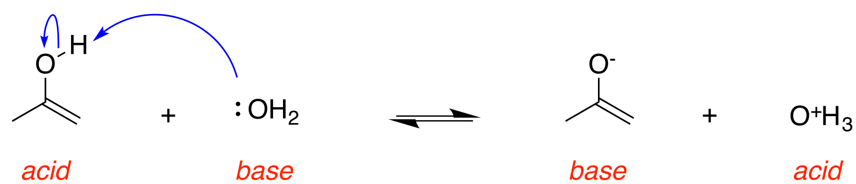
Weak acids have *higher* pK_a values than stronger acids.

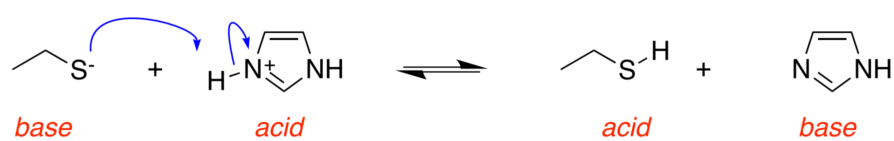
EtO^-	+	H_2O	$\rightleftharpoons$	EtOH	+	OH^-
base		*acid*		*acid*		*base*
MeOH	+	Me_3NH^+	$\rightleftharpoons$	$MeOH_2^+$	+	Me_3N
base		*acid*		*acid*		*base*
	+	H_2O	$\rightleftharpoons$		+	H_3O^+
acid		*base*		*base*		*acid*

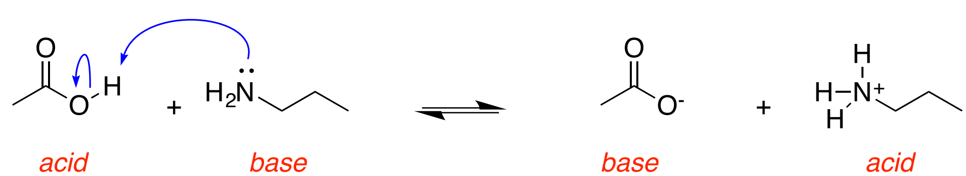


It *is* possible for the same compound to be an acid in some reactions and a base in others.







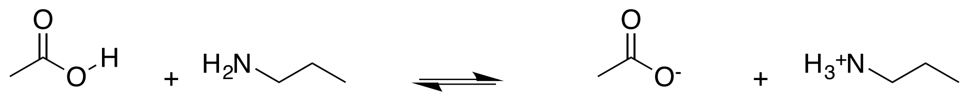


deprotonating an acid can be called its *conjugate base*.

given to the substance formed by *protonating a base*.

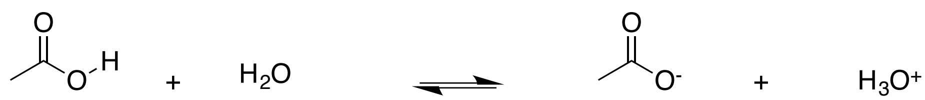
Ammonium, NH_4^+, is the conjugate *acid* of ammonia.

Hydroxonium is the conjugate *acid* of water.



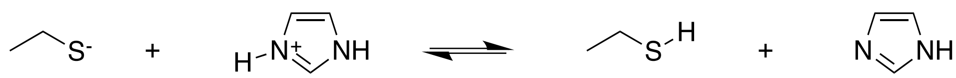
stronger *weaker*

favors *products*



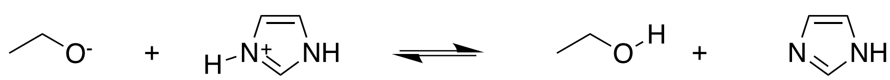
weaker *stronger*

favors *starting materials*



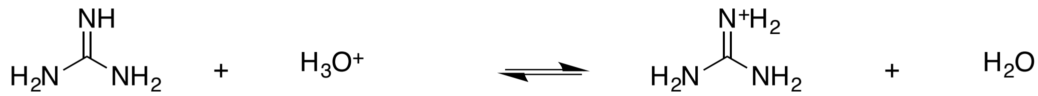
stronger *weaker*

favors *products*



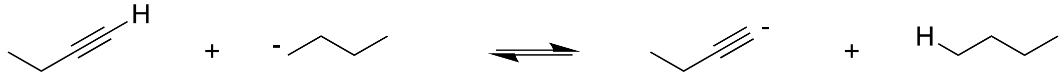
stronger *weaker*

favors *products*



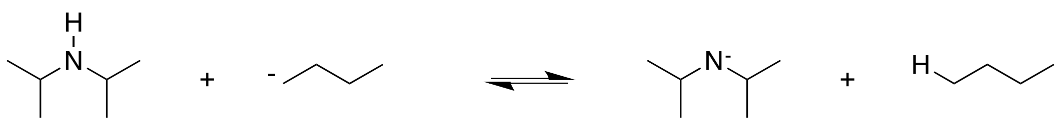
guanidine *stronger* *weaker*

favors *products*



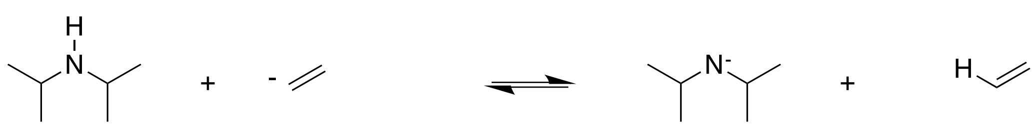
stronger *weaker*

favors *products*



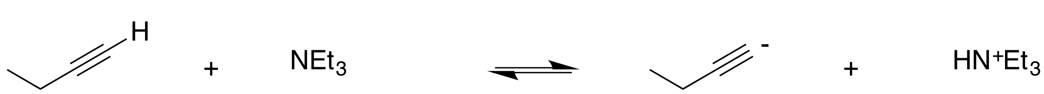
stronger *weaker*

favors *products*



stronger *weaker*

favors *products*



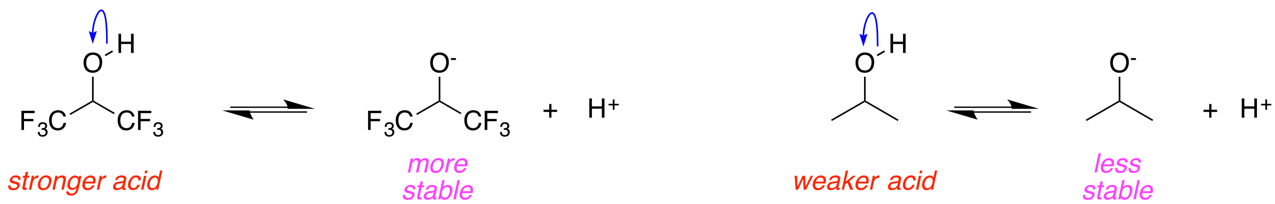
weaker *stronger*

favors *starting materials*

D. Predicting Relative pKₐ Values

Ethanoic acid is a *weaker* acid than trifluoroethanoic acid.

stabilized by *electronegativity* effects.

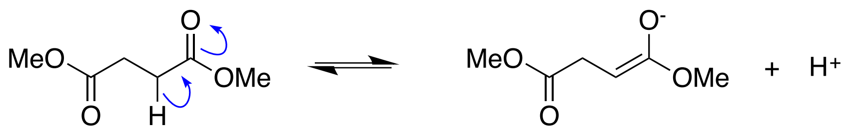


1,1,1,3,3,3-Hexafluoropropan-2-ol has a lower pK_a than propan-2-ol; therefore, it is a stronger acid.

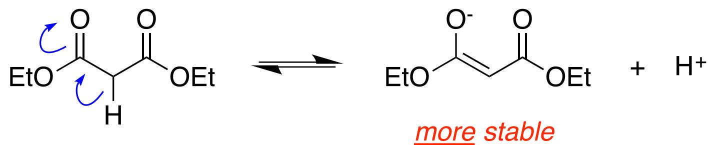
The alkoxide from 1,1,1,3,3,3-hexafluoropropan-2-ol is *more* stable than that from propan-2-ol because of *electronegativity* effects.

Allyl anions are *more* stable than propyl anions due to *resonance* effects, hence propene is a *stronger* acid than propane.

The enolate from ethanal is *more* stable than allyl anions due to *electronegativity* effects, so ethanal has a *lower* pK_a than propene.



less stable

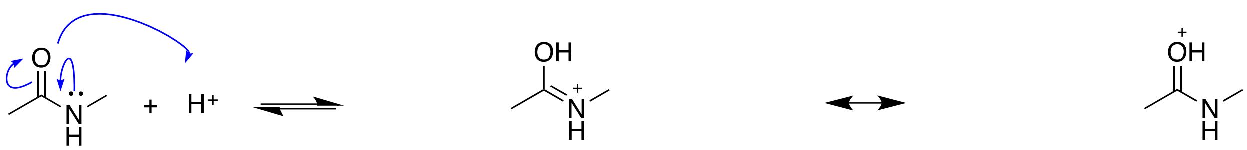


more stable

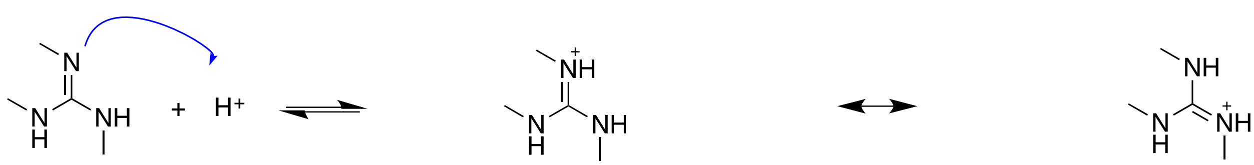
Dimethyl succinate has a *higher* pK_a than diethyl malonate, mainly due to *resonance* effects.

E. Predicting Sites Of Protonation

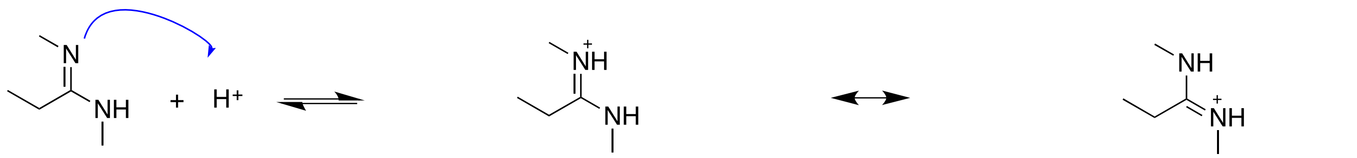
protonated form	*protonated form*



protonated form	*protonated form*

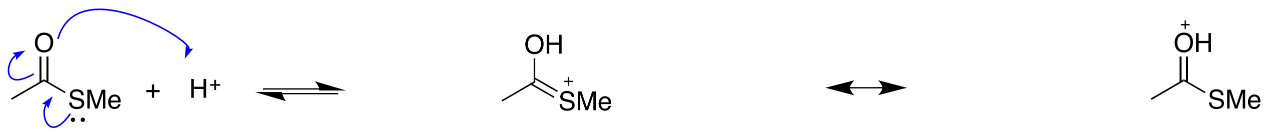


protonated form	*protonated form*



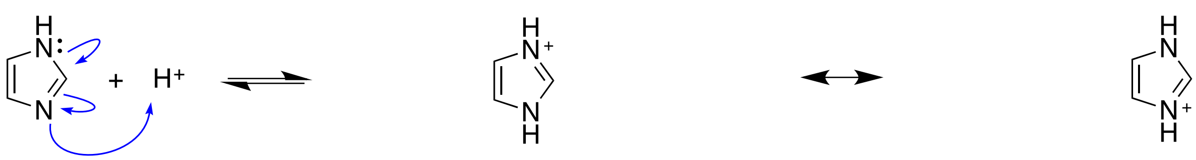
protonated form

protonated form



protonated form

protonated form



protonated form

protonated form

protonated form

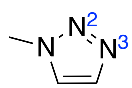
protonated form

protonated form

protonated form

most likely to be protonated selectively at *N^3*.

explanation:



because of resonance, electrons

can move from *N^1* to *N^3* another

F. Lewis Acids And Bases

Protons feature in *some* acids.

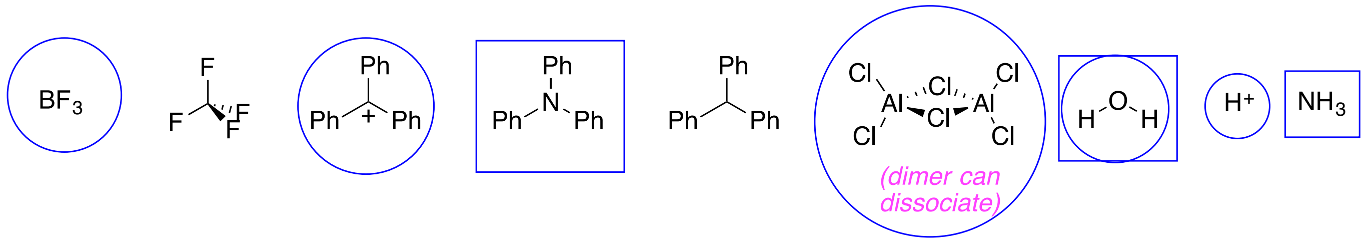
eg *an empty p-orbital*.

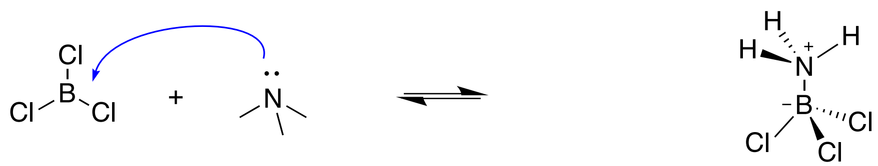
Lewis *acids*

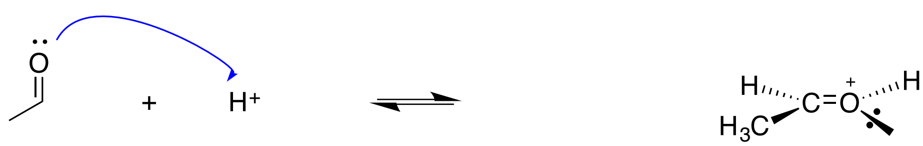
acids because they have *6* electrons in their valence shell and *an empty*

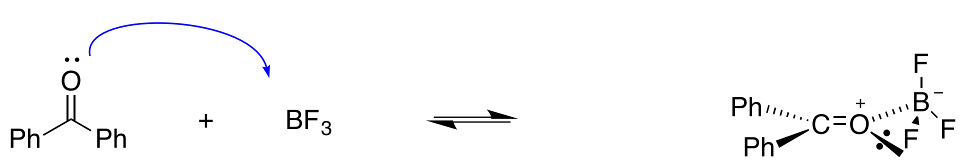
can fit the definition of a Lewis acid.

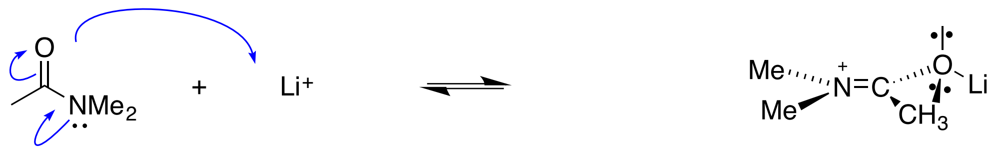
Protons *do* fit

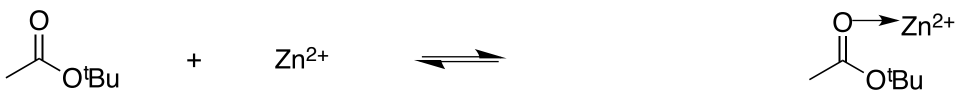

(dimer can dissociate)

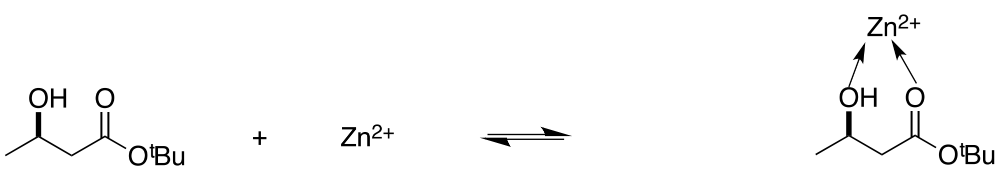












two phosphorus atoms are *sp*^{3} hybridized.