Acids And Bases

A. Introduction

.

B. Log Scales To Measure Proton Dissociation From Organic Molecules

Equilibria That Generate Protons

a *constant*, because an equilibrium
variable, therefore
is not a good parameter
will not change

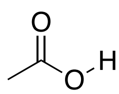
This *is* effectively the same as the statement:

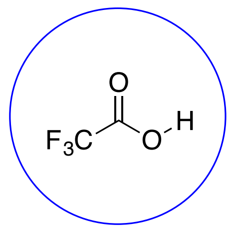
may be represented as:

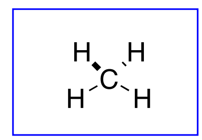
for *all* organic
a *small* fraction
a *strong* acid
is *high*.

weak acid.

therefore a significantly *stronger* acid than methane.

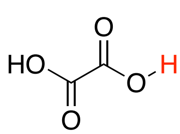


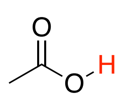


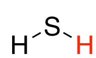


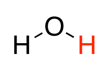
- *does*

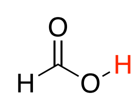
10^{60} 10^{6} 10 1 10^{-6} 10^{-60}

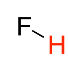












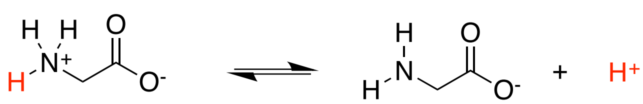
$K_a = 5.4 \times 10^{-2}$	1.8×10^{-5}	1.1×10^{-7}	1.0×10^{-14}	1.8×10^{-4}	6.6×10^{-4}
1	4	5	6	3	2

1 would be a *strong* acid.

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

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

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

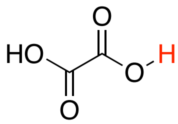
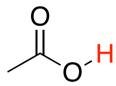
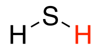
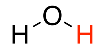
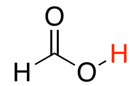
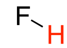


and $$[H^+] = \frac{K_a \; [^+NH_3CH_2CO_2^-]}{[NH_2CH_2CO_2^-]}$$

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

Simplifying The Scale: pKa

are *less* than the absolute differences

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

called the *pK_a* value.

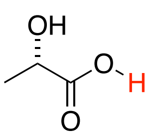
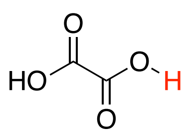
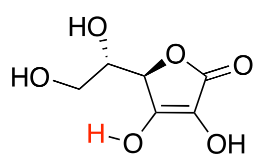
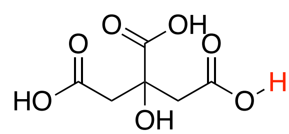
only a small amount of the compound

are *positive* for

larger K_a

less

smaller pK_a values.

			
lactic acid *pK_a = 3.86*	*oxalic acid* *4.19*	*ascorbic acid* *4.10*	*citric acid* *3.08*
2	4	3	1

10 times easier

10,000,000,000 times easier to

NH_4^+	NH_3	H_3O^+	H_2O
ammonium	*ammonia*	*hydroxonium*	*water*
pK_a = 9.2	*38*	*-1.7*	*15.7*
2	4	1	3

more

less likely that water will dissociate into hydroxide and a proton

C. Acid-Base Equilibria

starting materials

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

acid *base* *base* *acid*

side with the weakest acid because

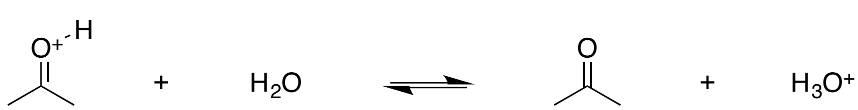
higher pK_a values

$$EtO^- + H_2O \rightleftharpoons EtOH + OH^-$$

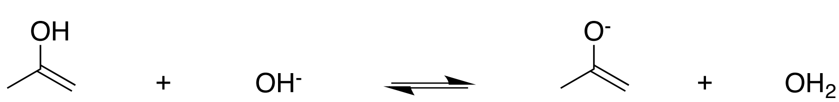
base *acid* *acid* *base*

$$MeOH + Me_3NH^+ \rightleftharpoons MeOH_2^+ + Me_3N$$

base *acid* *acid* *base*

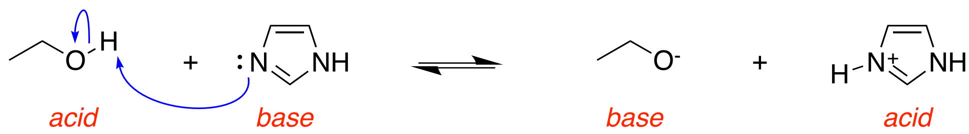


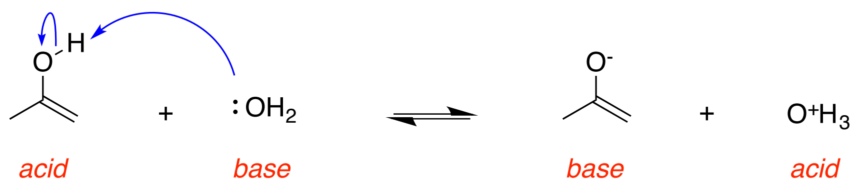
acid *base* *base* *acid*

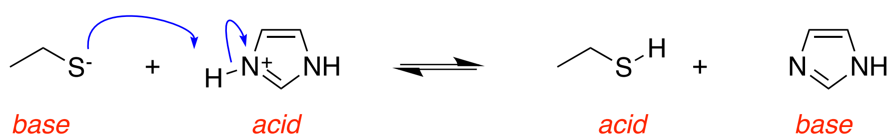


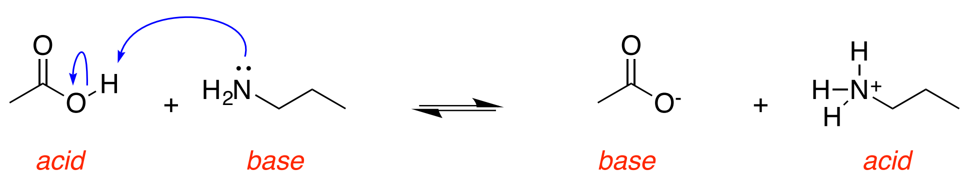
acid *base* *base* *acid*

It is possible for

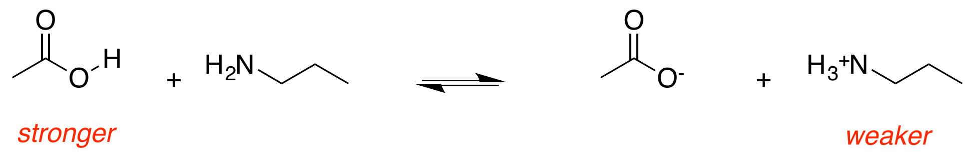




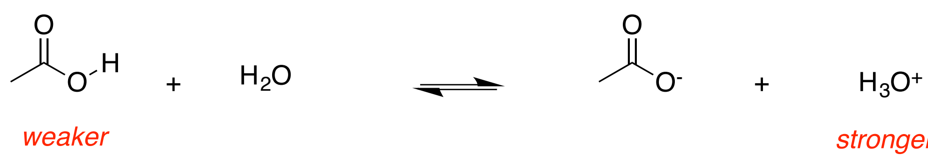




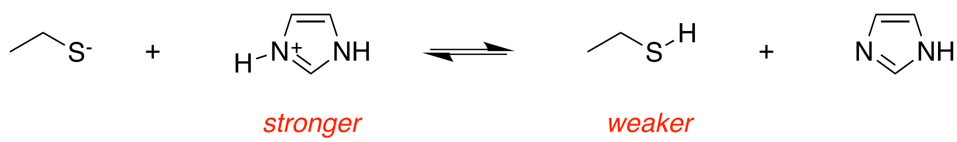
called its *conjugate base*.
formed by *protonating a base*.
acid of ammonia.
acid of water.



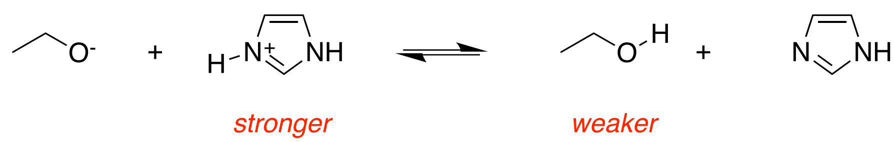
favors products



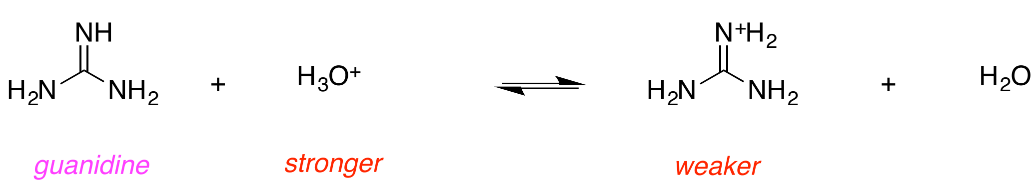
favors starting materials



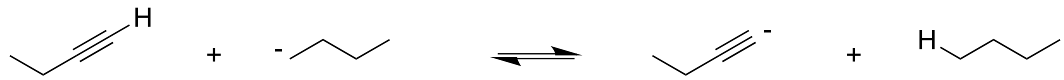
favors products



favors products

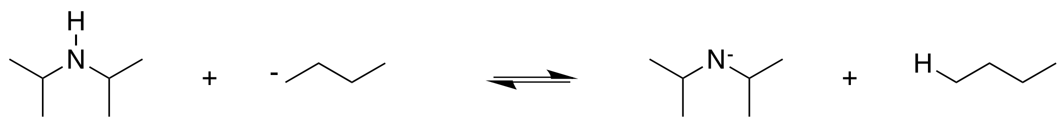


favors products



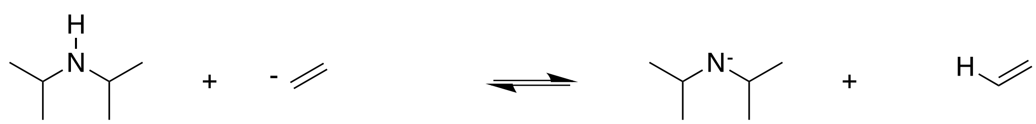
stronger *weaker*

favors *products*



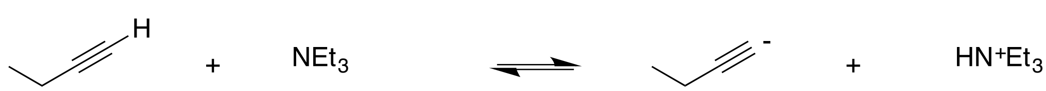
stronger *weaker*

favors *products*



stronger *weaker*

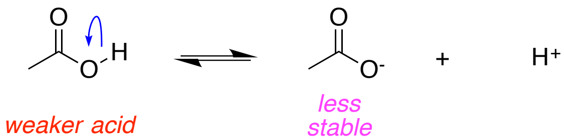
favors *products*

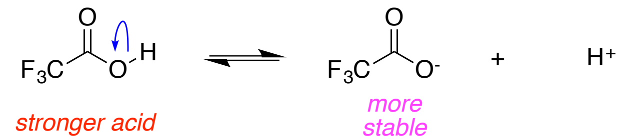


weaker *stronger*

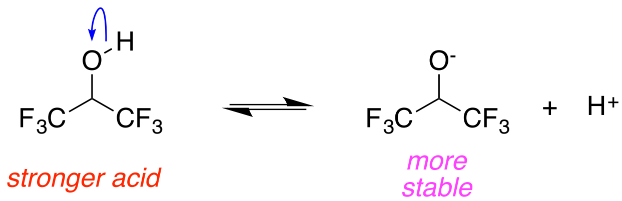
favors *starting materials*

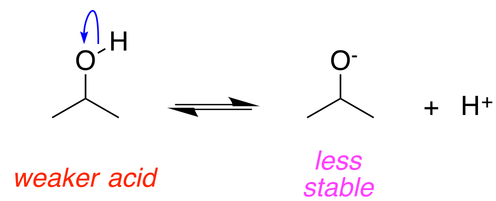
D. Predicting Relative pK_a Values





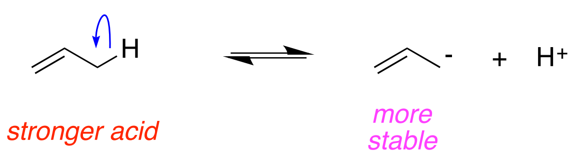
Ethanoic acid is a *weaker*
stabilized by *electronegativity*

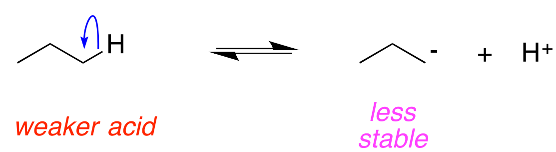




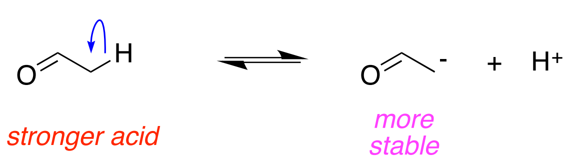
1,1,1,3,3,3-Hexafluoropropan-2-ol has a *lower* pK_a
stronger acid.

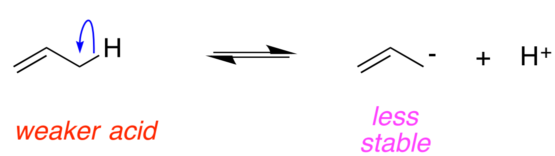
more stable than that from propan-2-ol because of *electronegativity* effects.



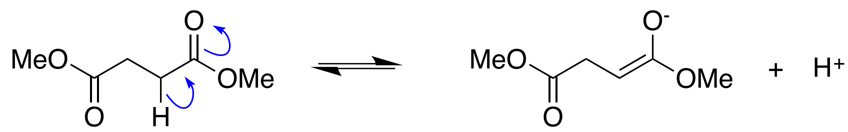


Allyl anions are *more* stable
resonance effects,
stronger acid than propane.

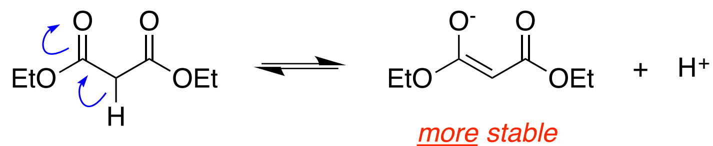




more stable than allyl anions due to *electronegativity* effects, so ethanal has a *lower* pK_a



less *stable*



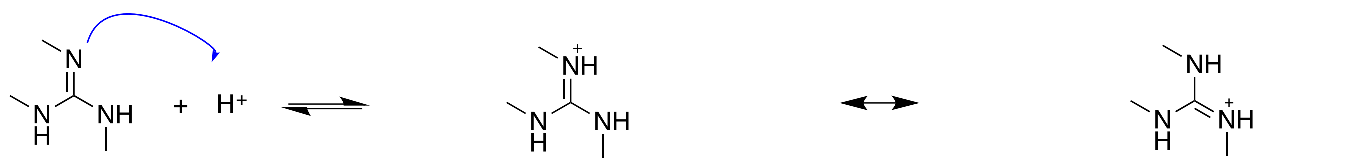
more *stable*

higher pK_a
resonance effects.

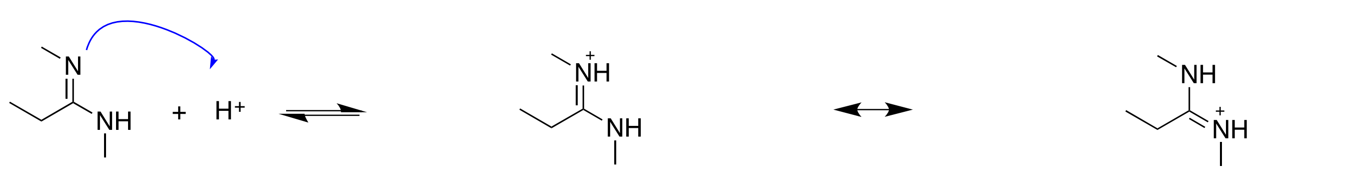
E. Predicting Sites Of Protonation

protonated form | *protonated form*

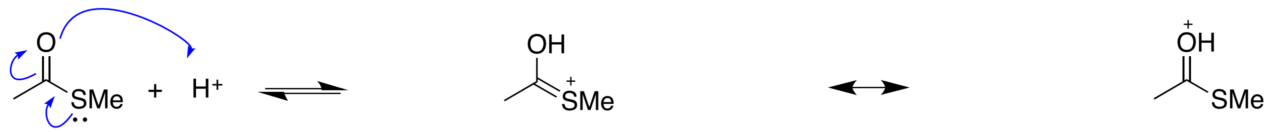
protonated form | *protonated form*



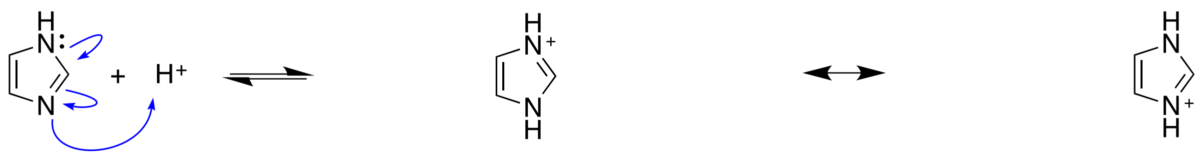
protonated form | *protonated form*



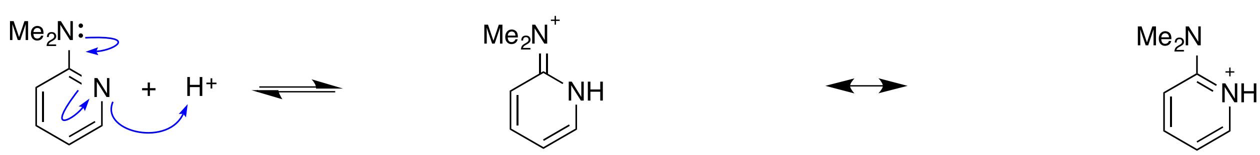
protonated form | *protonated form*



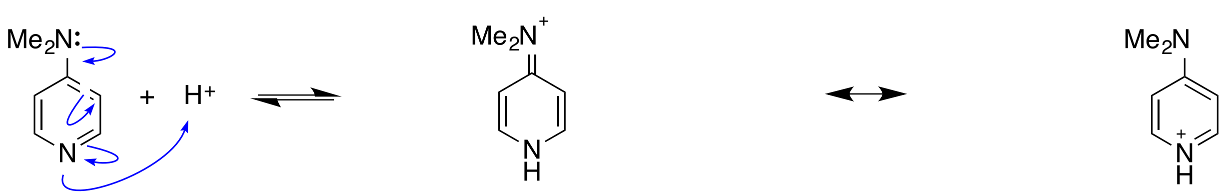
protonated form | protonated form



protonated form | protonated form

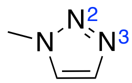


protonated form | protonated form



protonated form | protonated form

selectively at *N^3*.



explanation:

because of resonance effect, electrons

can move from one *N* to another

.

F. Lewis Acids And Bases

All acids *do not*

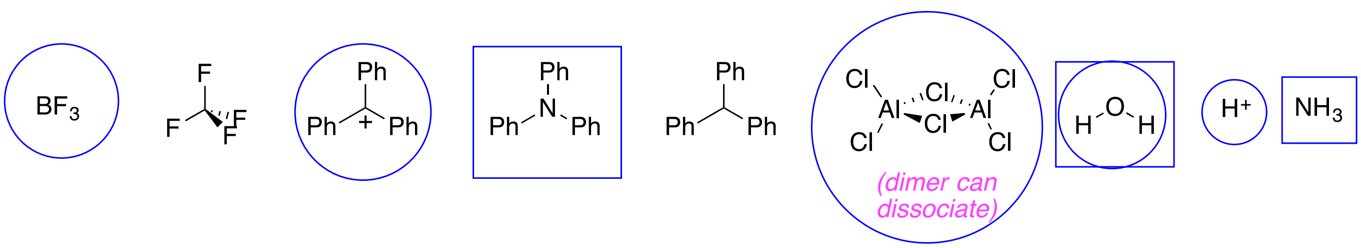
eg *an empty p-orbital*.

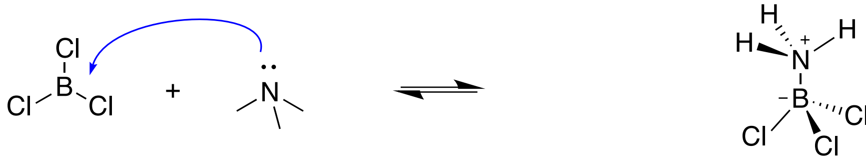
Lewis *acids*

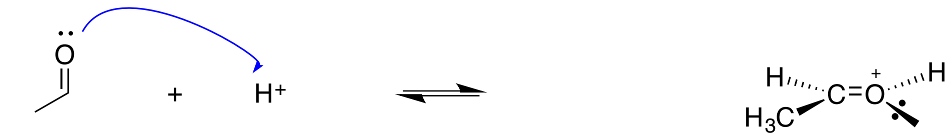
acids because they have *6* electrons in their valence shell and *an empty*

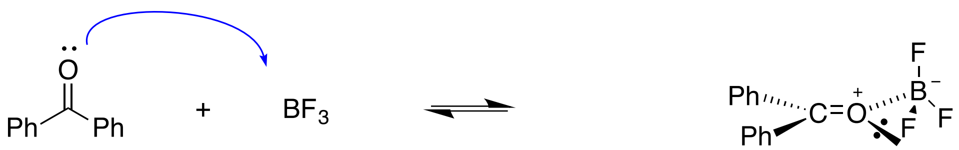
can fit the definition of a Lewis acid.

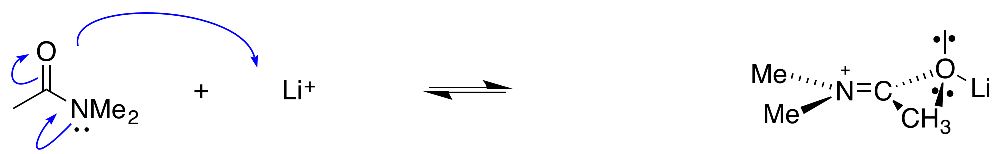
Protons *do* fit

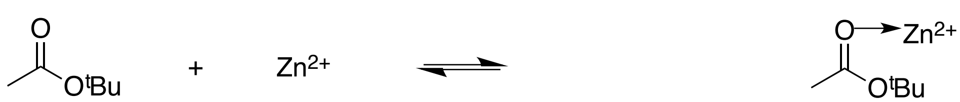


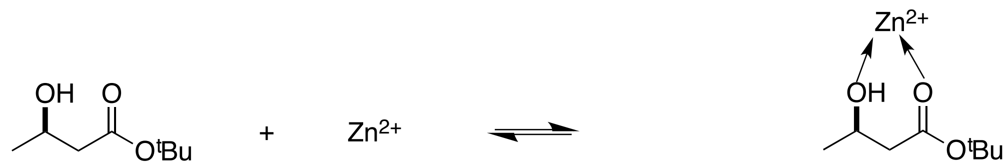



O
+
H+
H
H3C
C=O
H


O
Ph
Ph
+
BF3
Ph
Ph
C=O
B
F
F
F


O
NMe2
+
Li+
Me
Me
N=C
O
Li
CH3


O
OtBu
+
Zn2+
O
Zn2+
OtBu



OH
O
O^{t}Bu
+
Zn^{2+}
Zn^{2+}
OH
O
O^{t}Bu

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