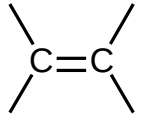
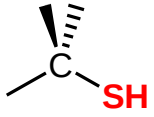
Gruppi funzionali in chimica bio-organica

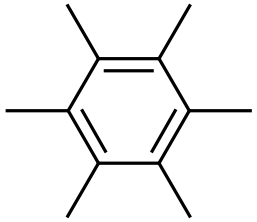
Un gruppo funzionale è una porzione della molecola, costituita da un gruppo di atomi, che presenta un comportamento chimico caratteristico.



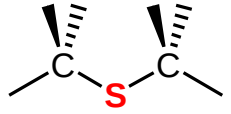
alchene
(doppio legame)



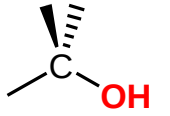
tiolo



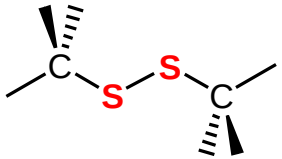
arene
(anello aromatico)



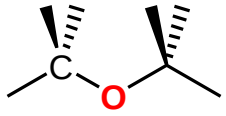
solfuro



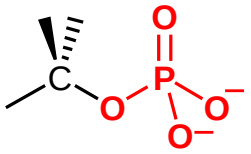
alcol



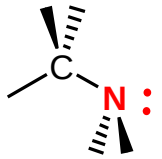
disolfuro



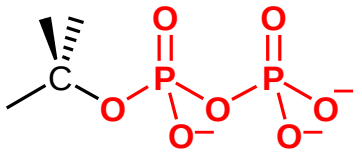
etere



fosfato

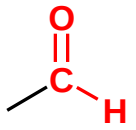


ammina

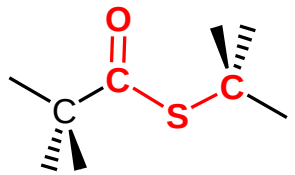


difosfato

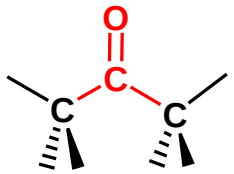
Gruppi funzionali in chimica bio-organica



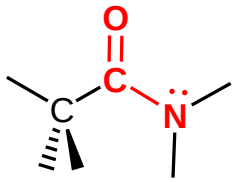
aldeide



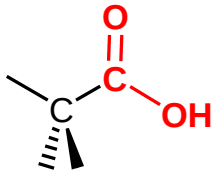
tioestere



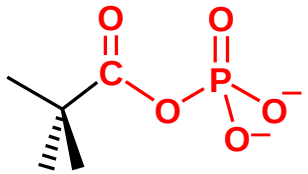
chetone



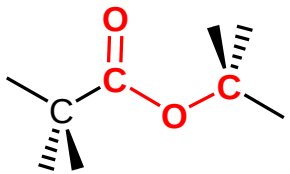
ammide



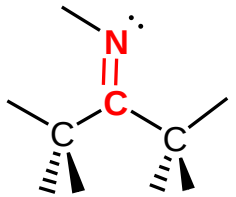
acido carbossilico



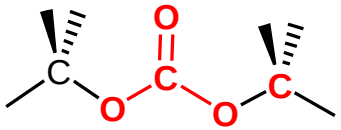
acilfosfato



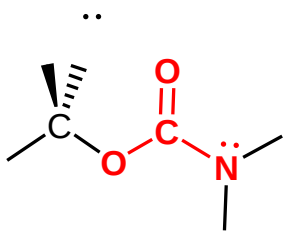
estere



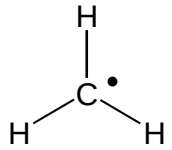
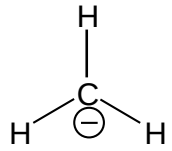
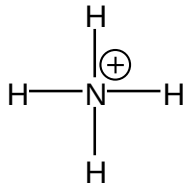
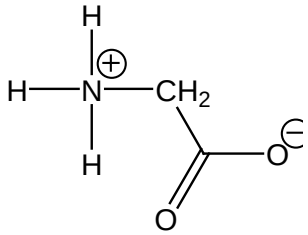
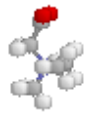
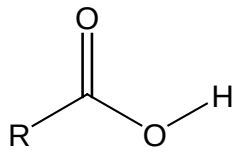
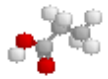
immina
(base di Shiff)

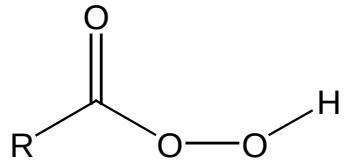
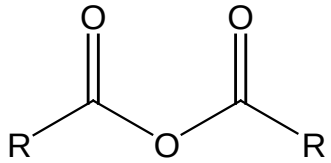
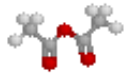
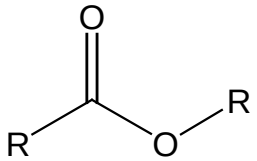
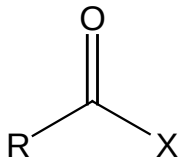
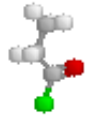
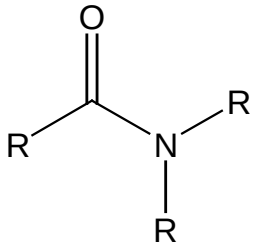
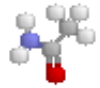


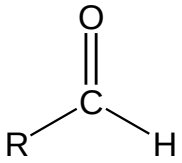
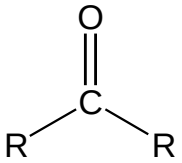
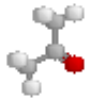
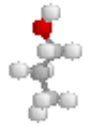
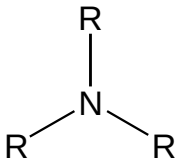
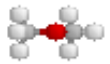
carbonato

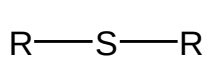
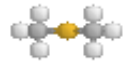
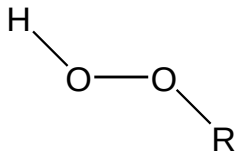
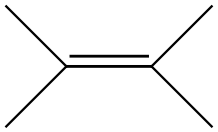
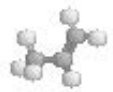
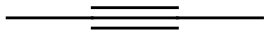
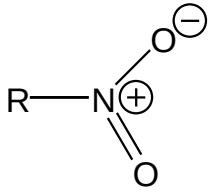
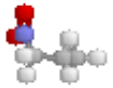


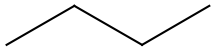
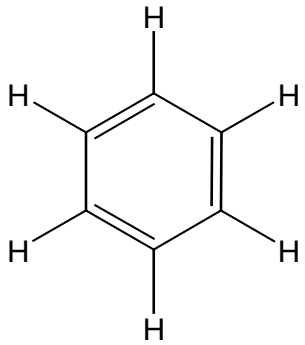
carbammato

Gruppo	Struttura a segmenti	suffisso o gruppo funzionale	prefisso	Struttura	Nome IUPAC
Radicali		-ile	----		metile
Anioni		-ide	----		metanide o metil anione
Cationi		-io es. -ammonio -fosfonio -ossonio -solfonio	ammonia- fosfonia- ossonia- sulfonia-		trimetilammonio
Zwitterioni		-io (per il catione) e -ide o -oato (per l'anione)	----		2-ammonio- N,N,N -trimetiletanoato
Acidi		Acido alcanoico	carbossi-		acido propanoico

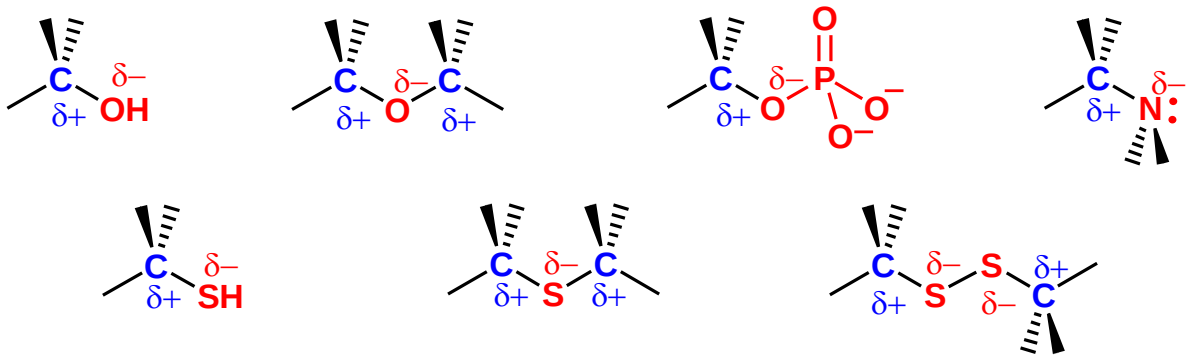
Perossi acidi		acido **perossi**alcan**oico**	idroperossicarbonile		acido perossietanoico
Anidridi		**anidride** alcan**oica**	-----		anidride alcanoica
Esteri		**alchil** alcan**oato**	alcossicarbonil- carbalcossi-		etil etanoate o etanoato di etile
Alogenuri acilici		Alcan**oil** **alogenuro**	aloalcanoil-		propanoil cloruro
Ammidi		-**ammide**	carbammoil-		etanammide
Nitrili		-nitrile -onitrile alchil cianuro	ciano-		propanonitrile o etil cianuro

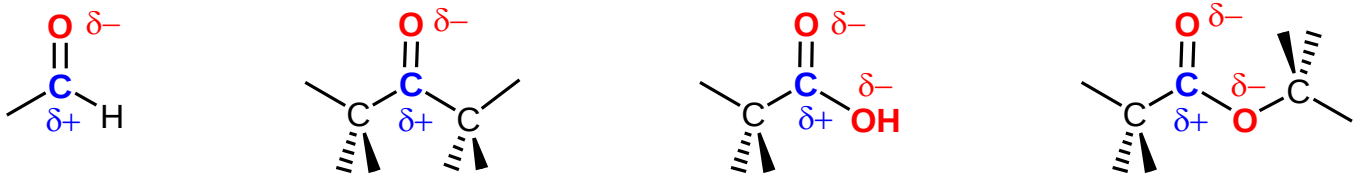
Aldeidi		-ale	alcanoil- -oxo-		propanale
Chetoni		-one alchil alchil chetone	-oxo- carbonile		propanone o dimetil chetone
Alcoli **(e Fenoli)**		-olo alcool alchilico	idrossi- (fenossi-)		propanolo o alcol propilico
Tioli		-tiolo alchil mercaptano	sulfanil- mercapto-		propantiolo
Ammine		-ammina	ammino- -aza-		propanammina
Eteri		alchil alchil etere	alcossi- -ossa-		dimetil etere

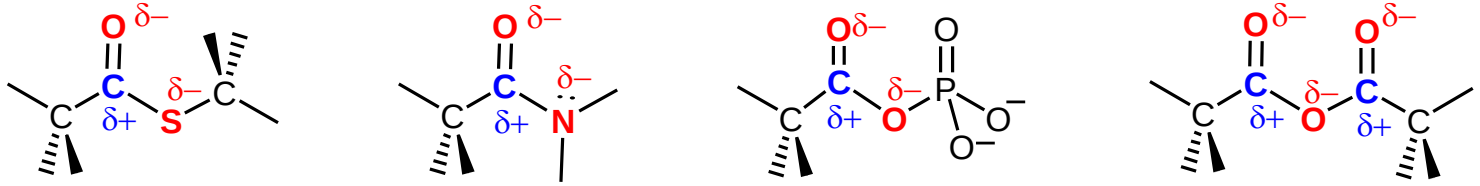
Solfuri		alchil alchil solfuro	-alchiltio -alchilsulfanil- -tia-		dimethyl sulfide
Perossidi		alchil idroperossido o alchil alchil perossico	idroperoddi- alchilperossi-		methyl hydroperoxide or hydroperoxymethane
Alcheni		-ene	alchenil-		propene
Alchini		-ino	alchinil-		propyne
Alogenuri		alogenuro alchilico	bromo- cloro- fluoro- iodo-		bromopropano or propil bromuro
Nitro		-----	nitro-		nitropropane

Alcani		-ano	-il alchil		propano
Areni o Aromatici (la priorità dipende dal gruppo funzionale presente sull'anello)		benzene	fenil		benzene

Polarizzazione dei legami dei gruppi funzionali



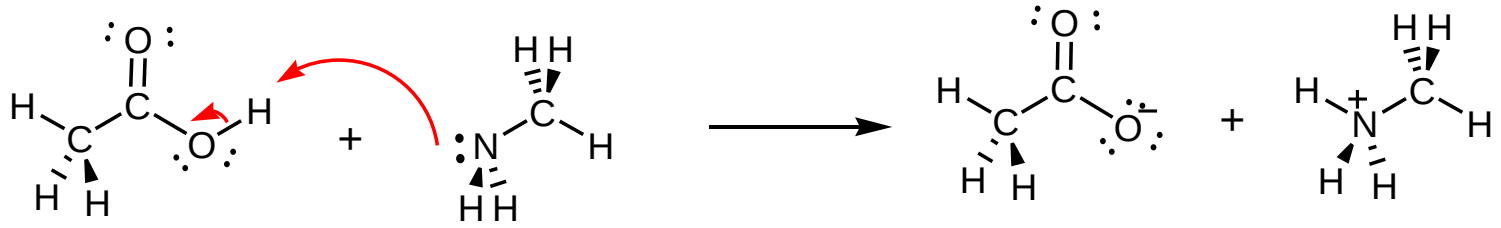




anidride

Acidi e basi di Brønsted-Lowry

Un **acido** è una sostanza in grado di donare un protone (ione idrogeno, H^+ o H_3O^+) e una **base** è una sostanza in grado di accettare un protone.



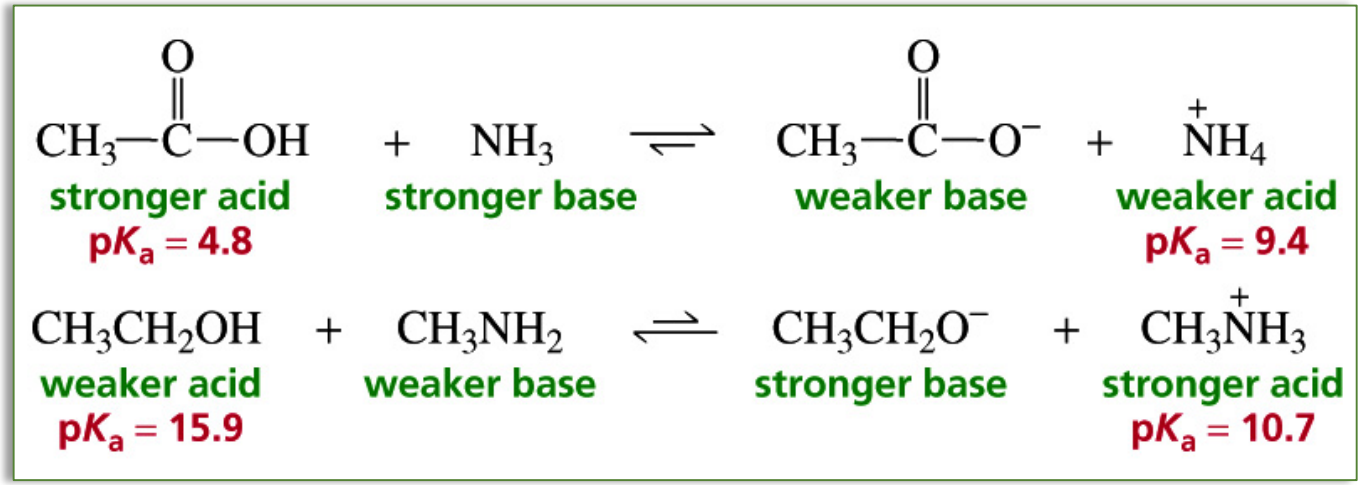
La forza di un acido **HA** in soluzione acquosa viene espressa dal pK_a, ossia dal logaritmo negativo della sua costante di acidità K_a

$$H_2O + HA \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

Acidi e basi di Brønsted-Lowry



$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

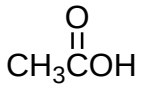
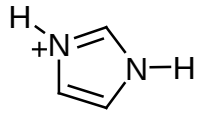
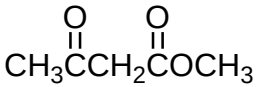
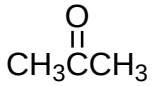
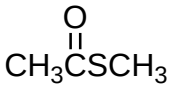
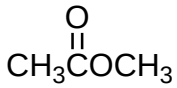
$$K_a = \frac{[B]\,[H_3O^+]}{[BH^+]}$$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$

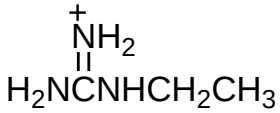
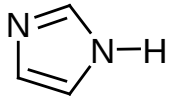
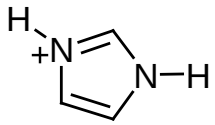
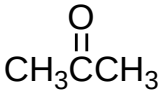
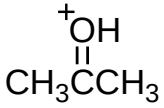
$$K_a \times K_b = \left(\frac{[B]\,[H_3O^+]}{[BH^+]}\right)\left(\frac{[BH^+]\,[OH^-]}{[B]}\right) = [H_3O^+]\,[OH^-] = K_w = 1.00 \times 10^{-14}$$

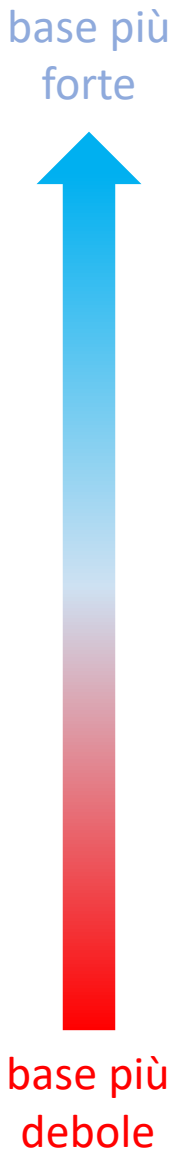
da cui $\quad pK_a + pK_b = 14$

Gruppo Funzionale	Esempio	pK_a
acido carbossilico		4.76
ione imidazolio		6.95
ione ammonio	NH_4^+	9.26
tiolo	CH_3SH	10.3
ione alchilammonio	$CH_3NH_4^+$	10.66
β-cheto estere		10.6
acqua	H_2O	15.75
alcol	CH_3OH	16.00
chetone		19.3
tioestere		21
estere		25

Acido più forte

Acido più debole

Gruppo Funzionale	Esempio		pK_a di BH^+
ione idrossido	OH^-	H_2O	15.75
guanidina			12.5
ammina	$CH_3NH_3^+$	CH_3NH_2	10.66
ammoniaca	NH_4^+	NH_3	9.26
imidazolo			6.95
acqua	H_2O	H_3O^+	-1.74
alcol	CH_3OH	$CH_3OH_2^+$	-2.05
chetone			-7.5



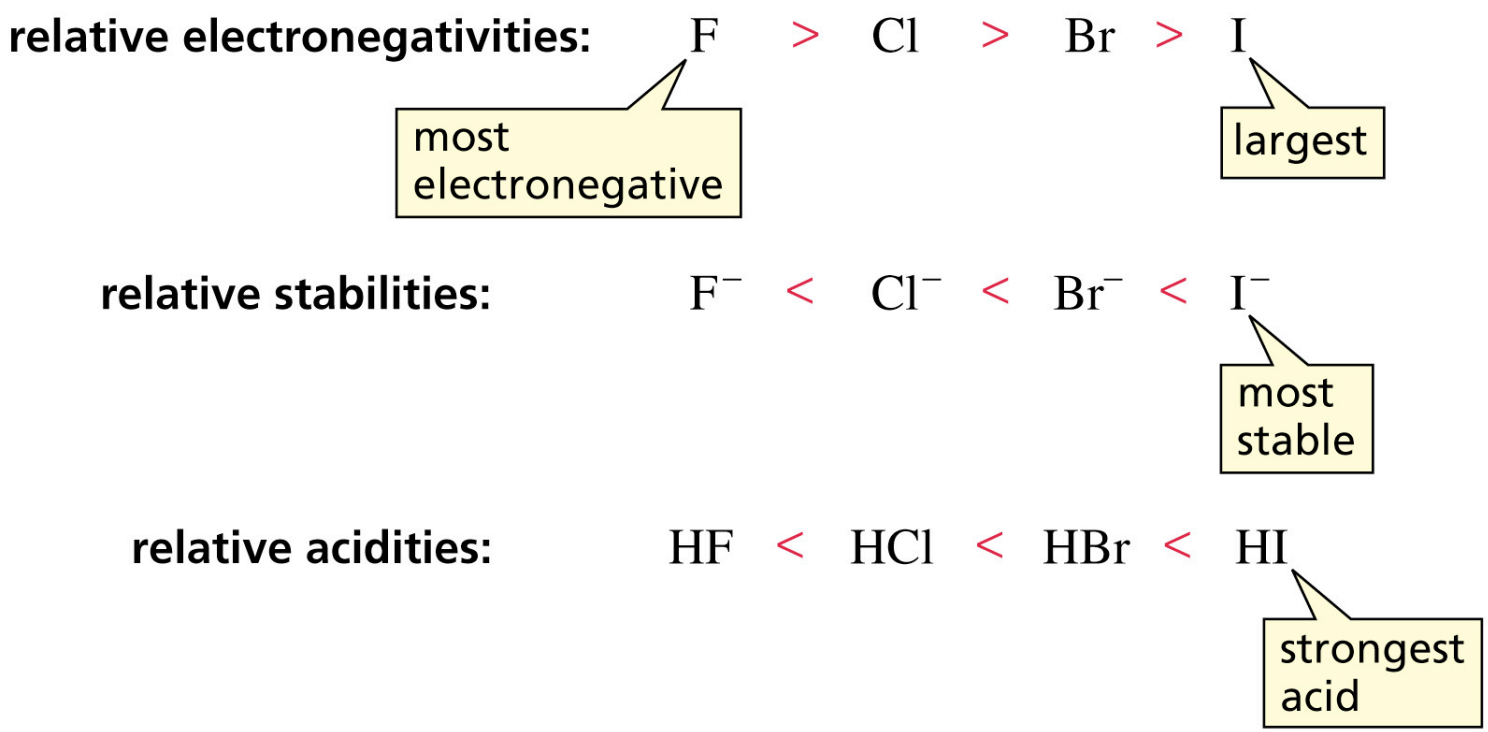
The Henderson–Hasselbalch Equation

The pH indicates the concentration of hydrogen ions (H^+)

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

- A compound will exist primarily in its acidic form at a pH < its pK_a
- A compound will exist primarily in its basic form at a pH > its pK_a
- A buffer solution maintains a nearly constant pH upon addition of small amount of acid or base

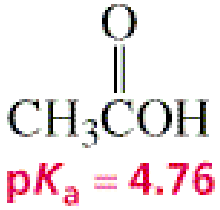
- When atoms are very different in size, the stronger acid will have its proton attached to the largest atom



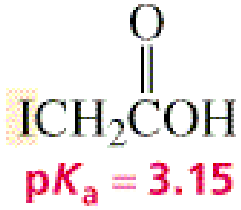
- When atoms are similar in size, the stronger acid will have its proton attached to the more electronegative atom

CH_3OH	CH_3NH_2
methanol	**methylamine**
$pK_a = 15.5$	**$pK_a = 40$**

- Inductive electron withdrawal increases the acidity of a conjugate acid

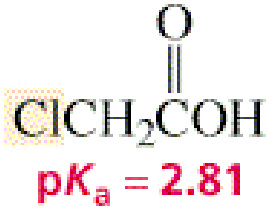


$pK_a = 4.76$

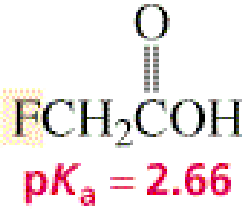


$pK_a = 3.15$

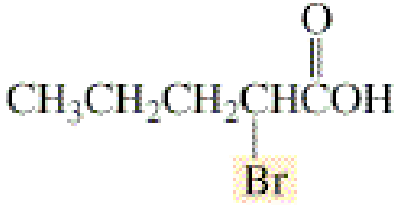
$pK_a = 2.86$



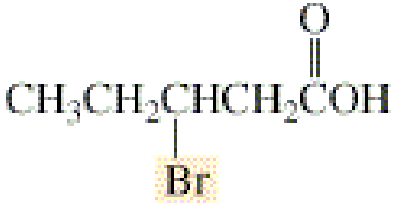
$pK_a = 2.81$



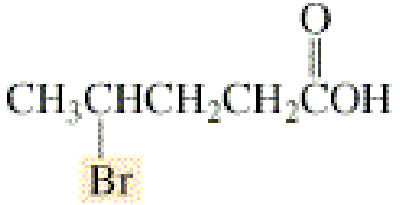
$pK_a = 2.66$



$pK_a = 2.97$



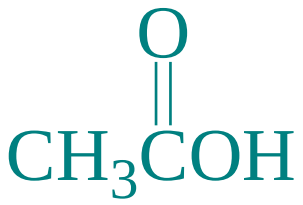
$pK_a = 4.01$



$pK_a = 4.59$

$pK_a = 4.71$

Acetic acid is more acidic than ethanol



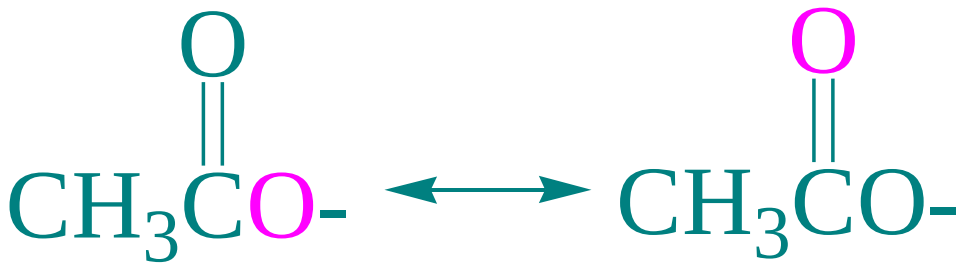
$pK_a = 4.76$

acetic acid

$pK_a = 15.9$

ethanol

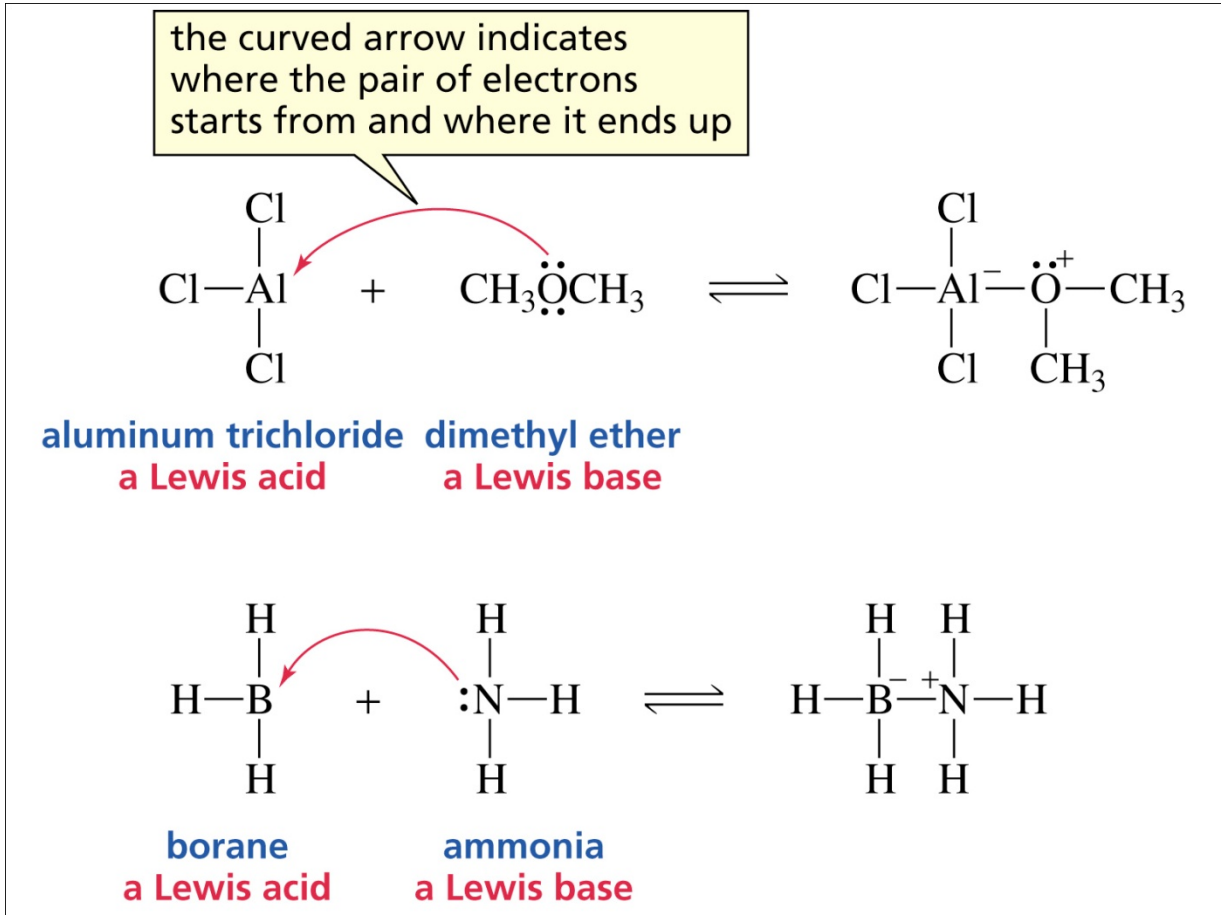
The delocalized electrons in acetic acid are shared by more than two atoms, thereby stabilizing the conjugated base

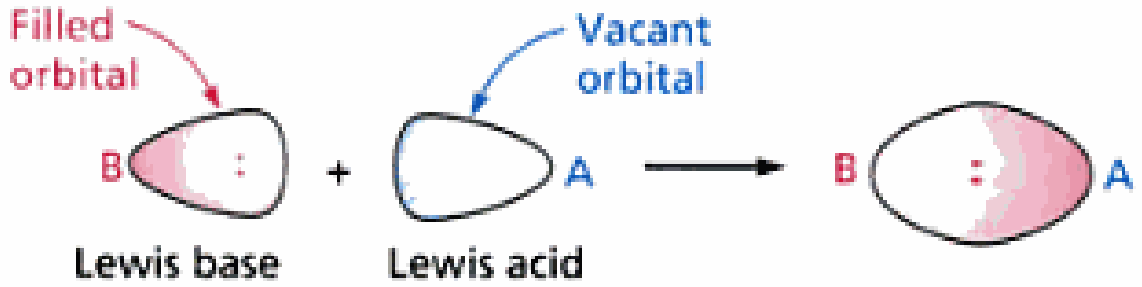


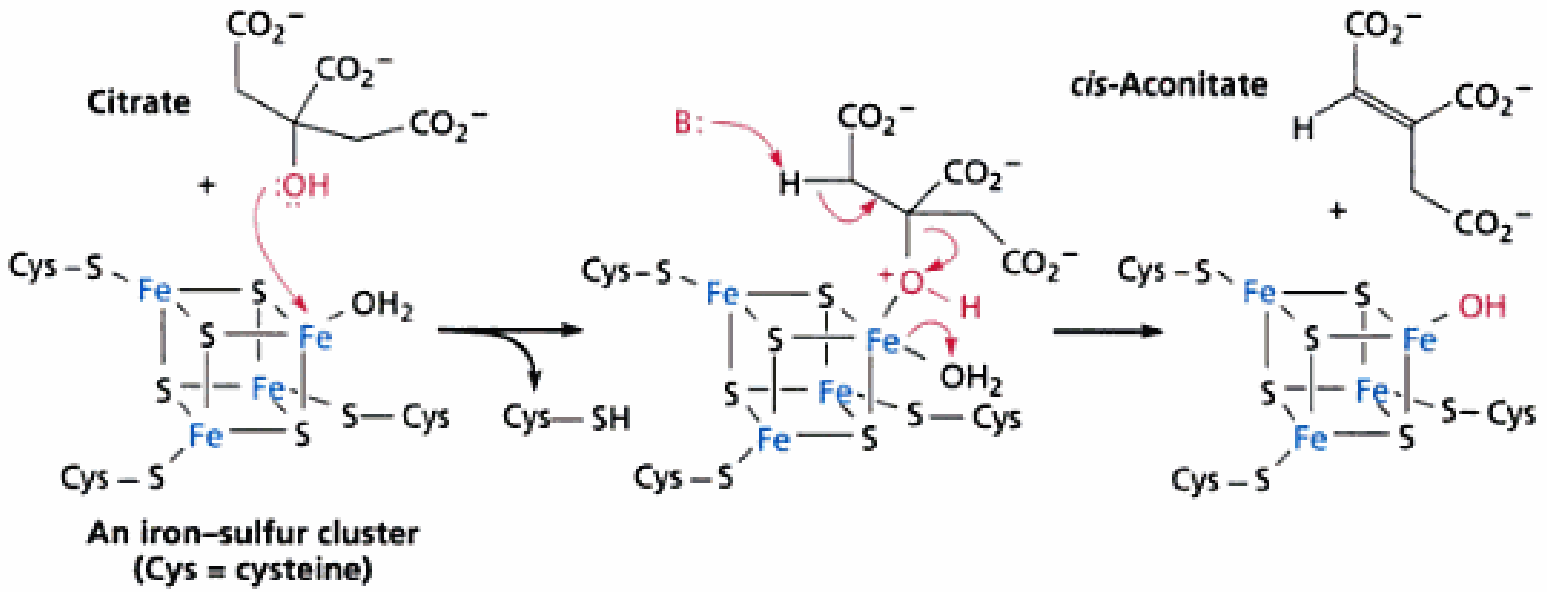
Acidi e basi di Lewis

- acido di Lewis : acido che non dona protoni; accetta elettroni

- base di Lewis : donatore di una coppia di elettroni

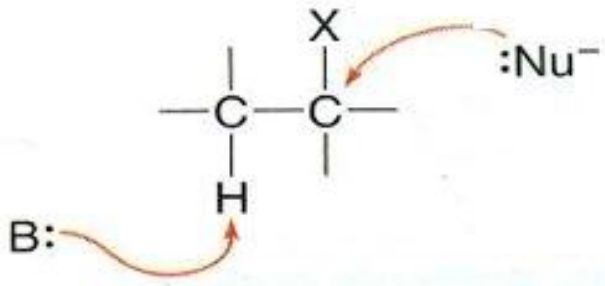



Filled orbital
Vacant orbital
B
A
+
B
A
Lewis base
Lewis acid


Citrate
+
:OH
Cys – S
Fe
S
OH2
Cys
Cys – SH
An iron–sulfur cluster
(Cys = cysteine)
B:
H
+O
H
cis-Aconitate
OH

CONFRONTO TRA NUCLEOFILICITÀ E BASICITÀ

La basicità è una misura di quanto prontamente un atomo dona la sua coppia di elettroni al protone ed è una proprietà termodinamica.



La nucleofilicità è invece la misura di quanto prontamente un atomo dona la coppia di elettroni ad atomi diversi da H^+. E' una proprietà cinetica

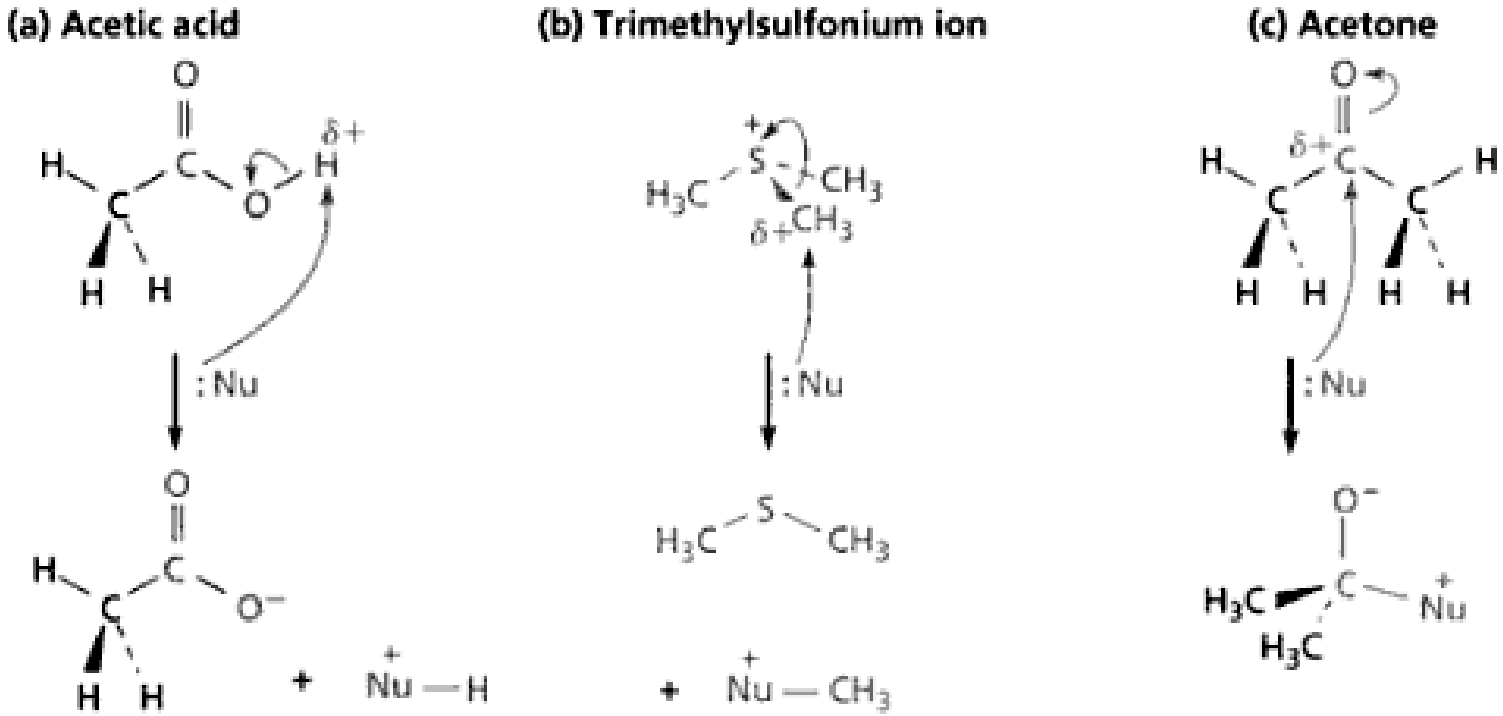


FIGURE 1.3 Some electrophiles and their reactions with nucleophiles (:Nu).