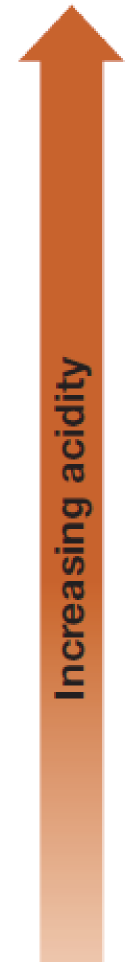
$$\mathrm{HA} + \mathrm{H_2O} \overset{K}{\rightleftharpoons} \mathrm{H_3O^+} + \mathrm{A^-} \qquad K = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}][\mathrm{H_2O}]}$$

$$K_\mathrm{a} = K[\mathrm{H_2O}] = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}\ \mathrm{mol\ L^{-1}}$$

pK_a = - log K_a

Acid	K_a	pK_a
Hydrogen iodide, HI (strongest acid)	$\sim 1.0 \times 10^{10}$	−10.0
Hydrogen bromide, HBr	$\sim 1.0 \times 10^{9}$	−9.0
Hydrogen chloride, HCl	$\sim 1.0 \times 10^{8}$	−8.0
Sulfuric acid, H_2SO_4	$\sim 1.0 \times 10^{3}$	−3.0[a]
Hydronium ion, H_3O^-	50	−1.7
Nitric acid, HNO_3	25	−1.4
Methanesulfonic acid, CH_3SO_3H	16	−1.2
Hydrogen fluoride, HF	6.3×10^{-4}	3.2
Acetic acid, CH_3COOH	2.0×10^{-5}	4.7
Hydrogen cyanide, HCN	6.3×10^{-10}	9.2
Ammonium ion, NH_4^+	5.7×10^{-10}	9.3
Methanethiol, CH_3SH	1.0×10^{-10}	10.0
Methanol, CH_3OH	3.2×10^{-16}	15.5
Water, H_2O	2.0×10^{-16}	15.7
Ammonia, NH_3	1.0×10^{-35}	35
Methane, CH_4 (weakest acid)	$\sim 1.0 \times 10^{-50}$	~50



Note: $K_a = [H_3O^+][A^-]/[HA]$ mol L^{-1}.

[a]First dissociation equilibrium

- pK_a kyseliny závisí na stabilitě její konjugované báze
- čím silnější HA, tím slabší A^-
- čím silnější A^- , tím slabší AH

silná kyselina

konjugovaná báze je slabá

slabá kyselina

konjugovaná báze silná

Jak zjistit relativní kyselost nebo bazicitu ze struktury látky

1. Který atom nese náboj?

Increasing electronegativity of A

H_4C H_3N H_2O HF

Increasing acidity

Hydrid	H-CH_3	H-NH_2	H-OH	H-F
pK_a	55	35	15.7	3.2

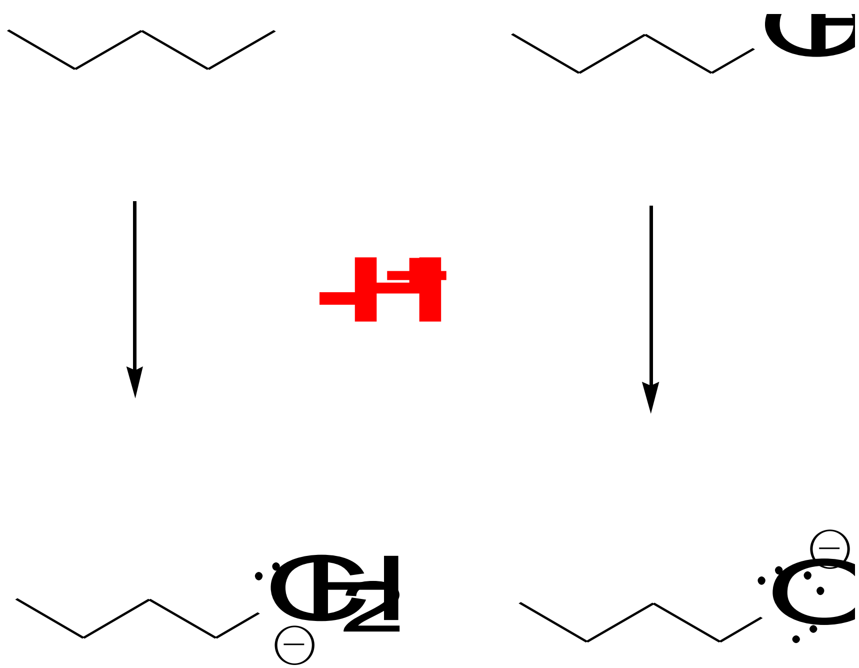
čím elektronegativnější prvek záporný náboj nese, tím je konjugovaná báze stabilnější

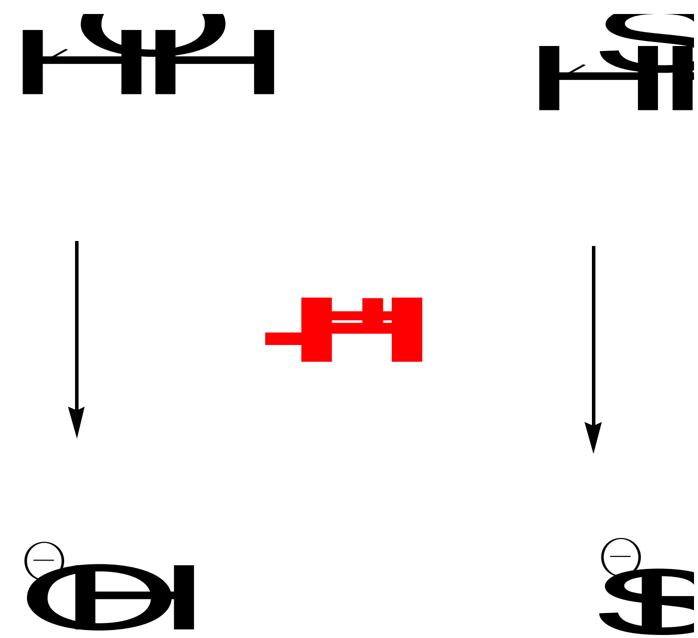
Increasing size of A

HF HCl HBr HI

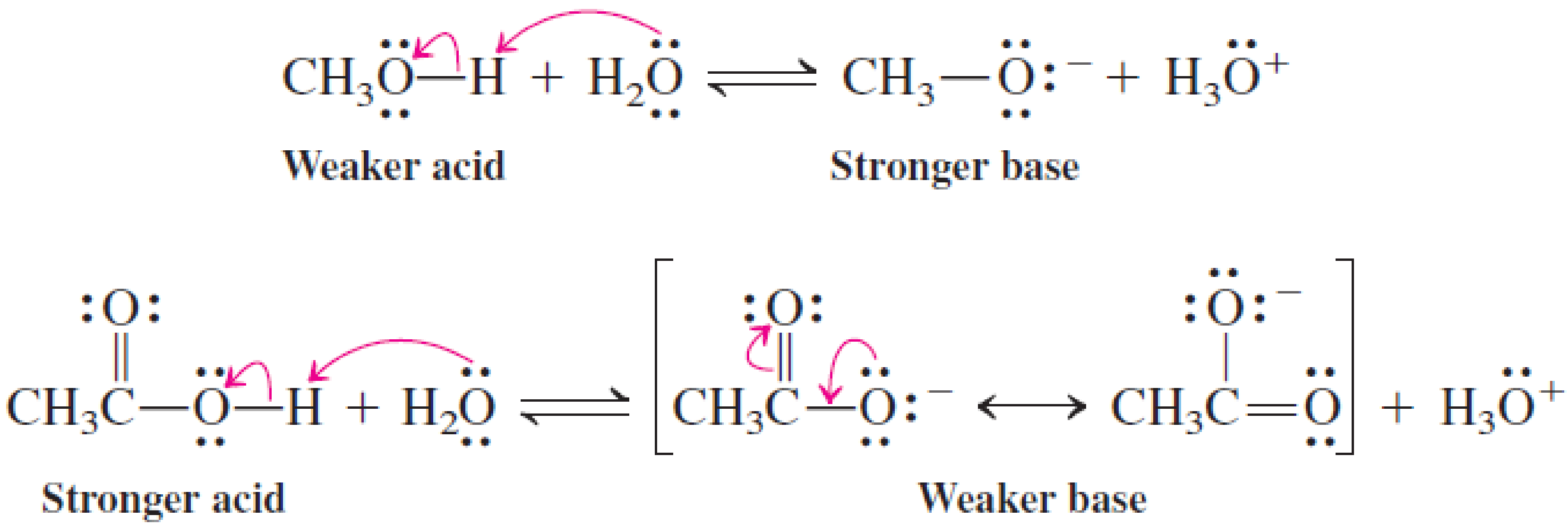
Increasing acidity

HX	pK_a	HX	pK_a
HF	3.2	ROH	15-16
HCl	–7	RSH	10
HBr	–9	RSeH	-
HI	–9.5	RTeH	7



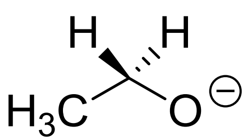


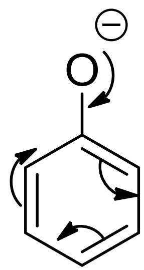
2. Delokalizace náboje v A^- - stabilizace

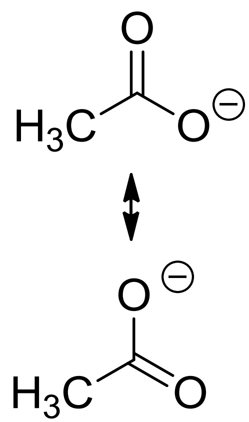


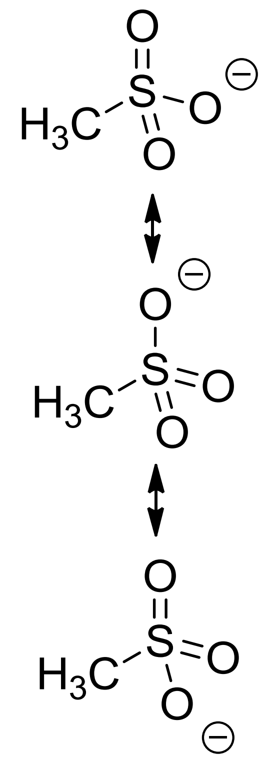
» delokalizace

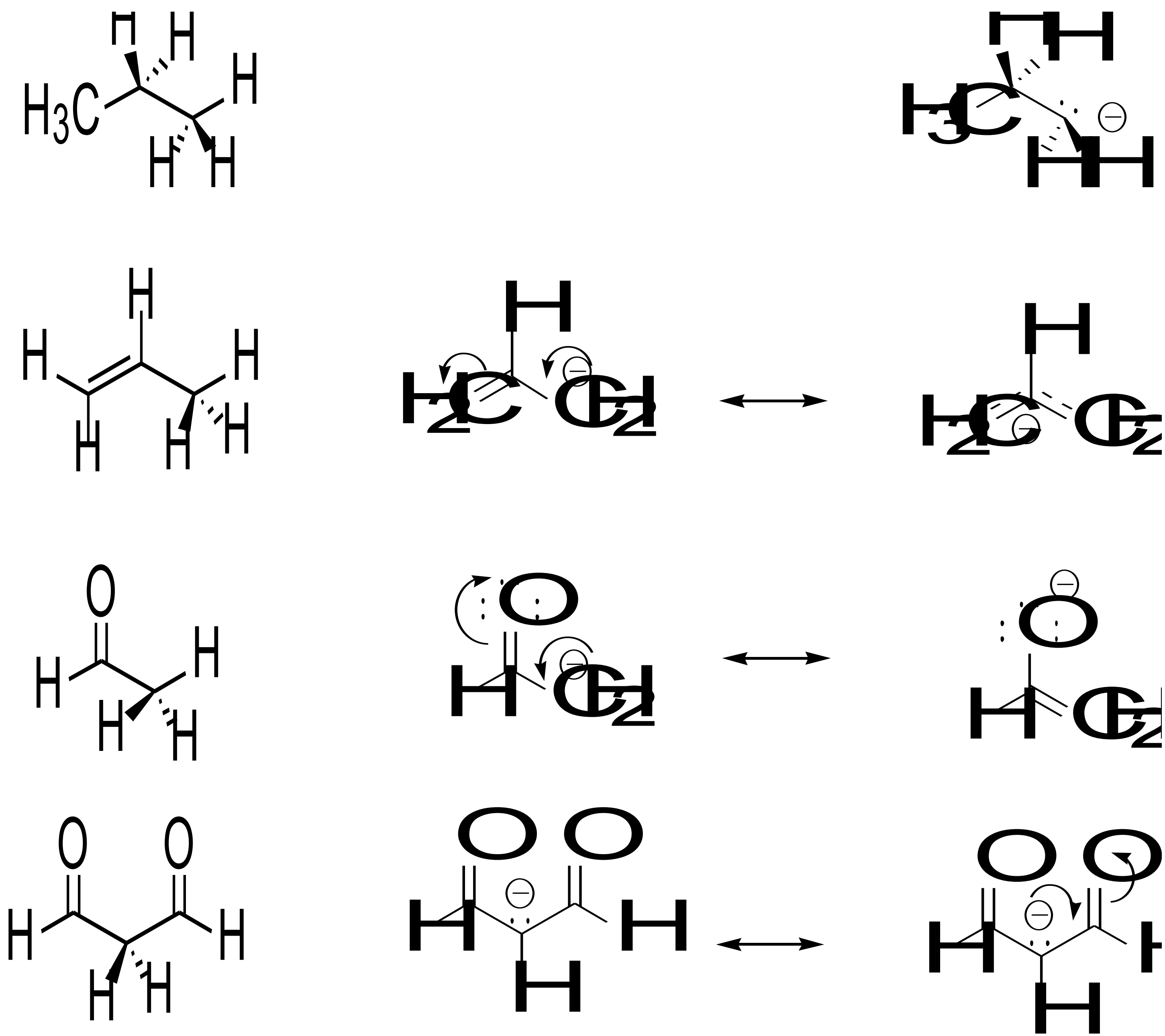
	EtOH	PhOH	CH_3COOH	CH_3SO_3H
p*K*$_a$	16	10	4,8	- 1,7

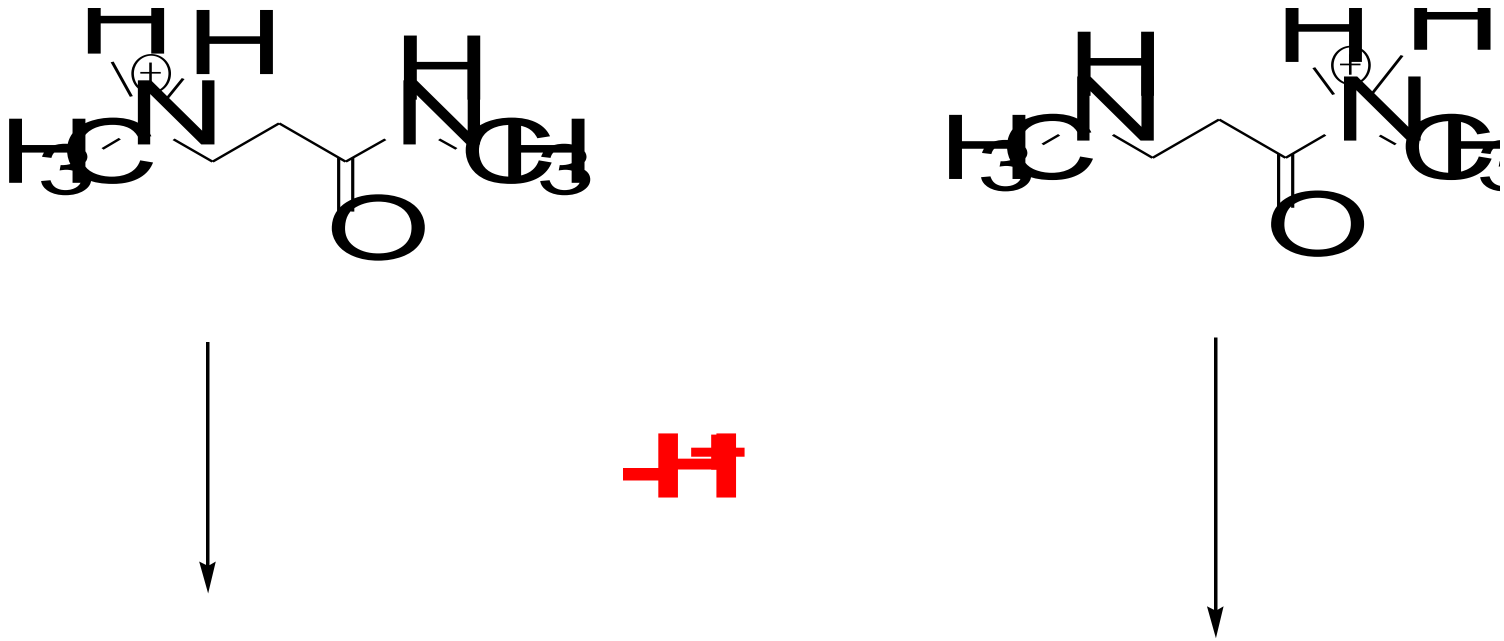




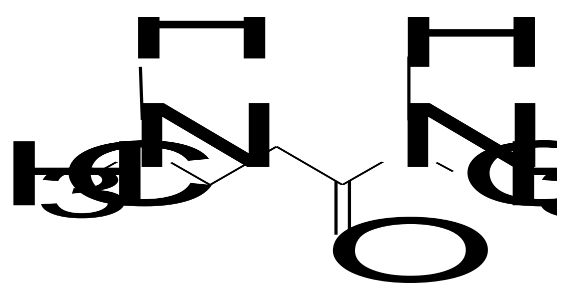






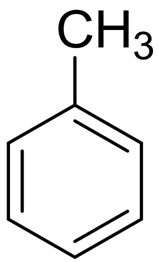


silnější kyselina
konjugovaná báze je
stabilizovaná
rezonanací

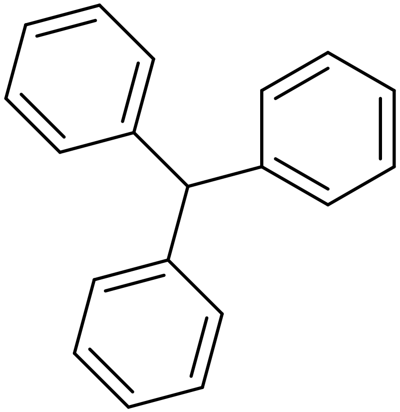


Amidy jsou slabé báze

Uvedené sloučeniny seřaďte podle vzrůstající kyselosti

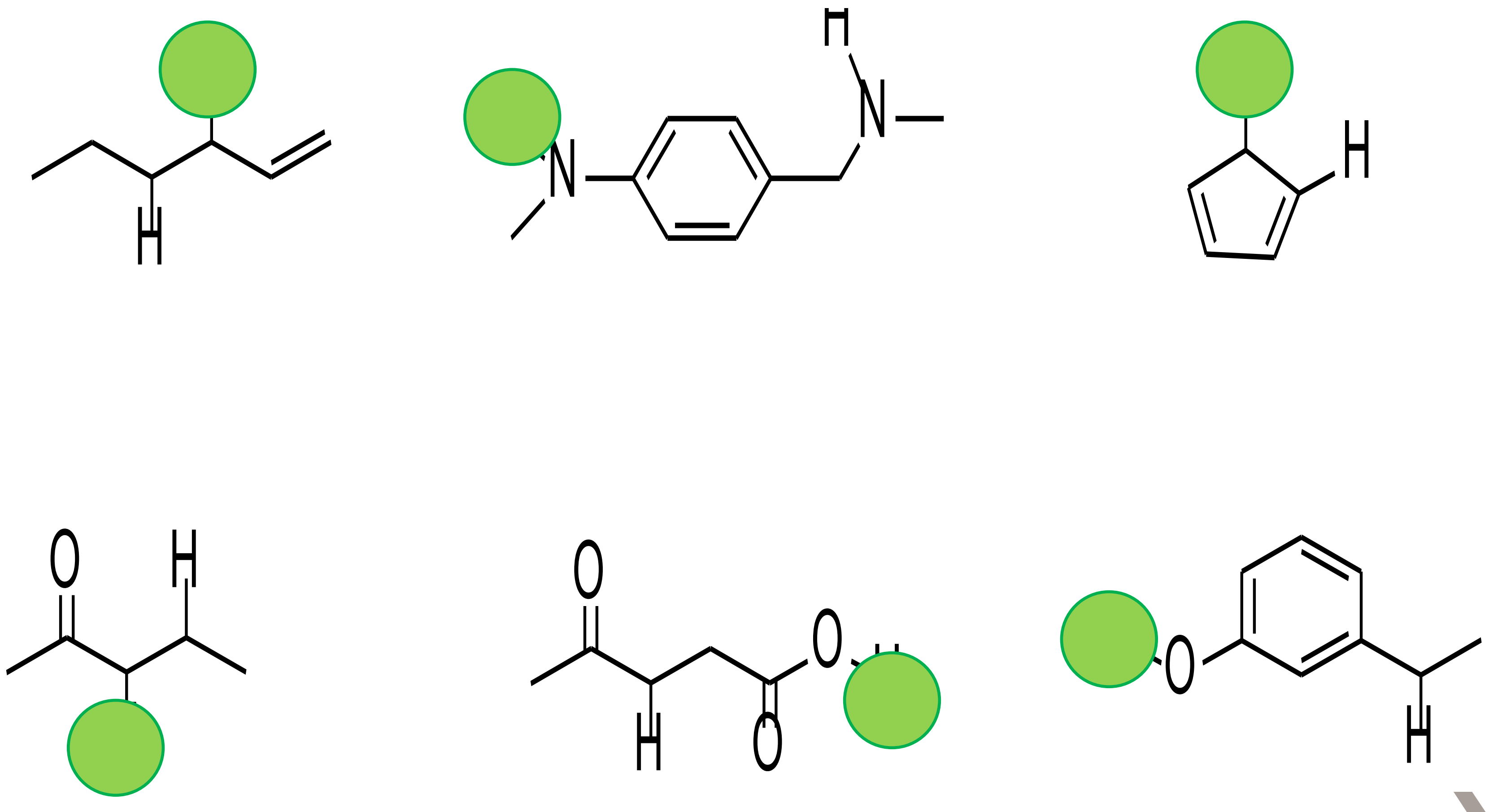


CH_4

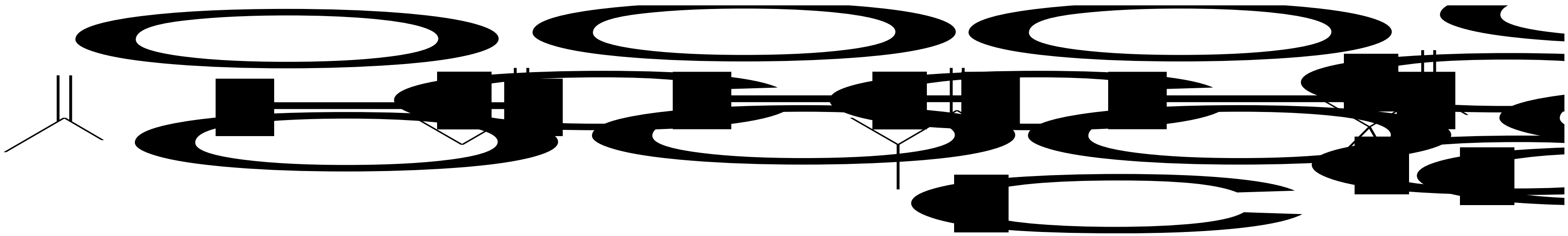


p*Ka*	40	48	32

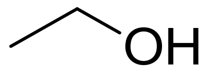
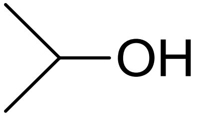
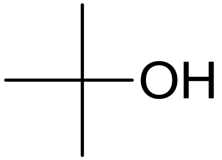
Který z vodíkových atomů v uvedené dvojici je kyselejší

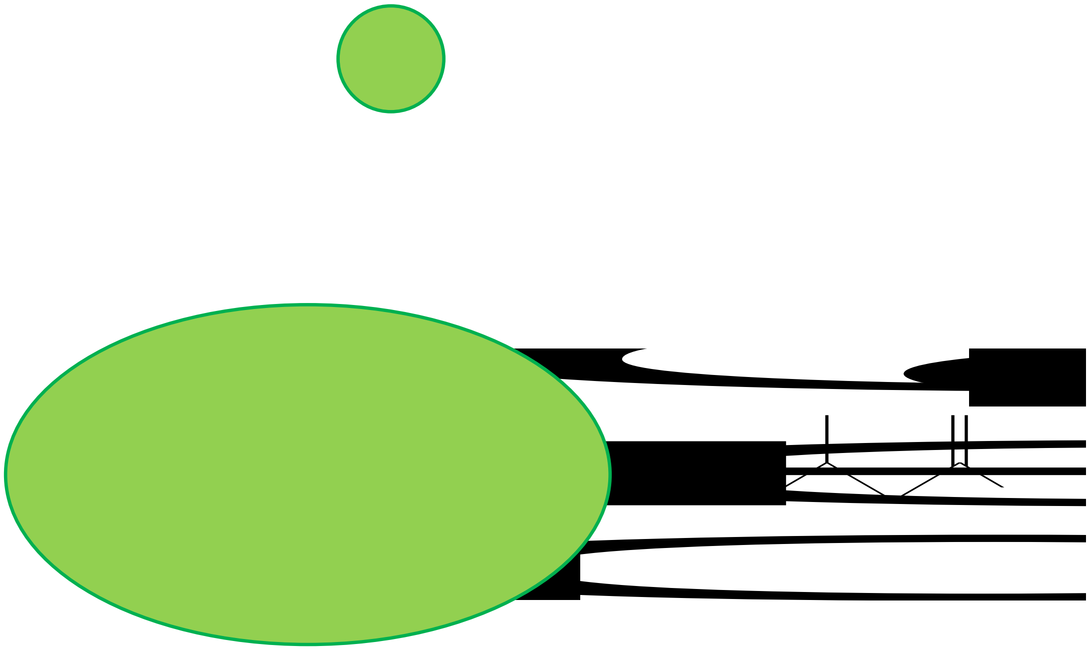


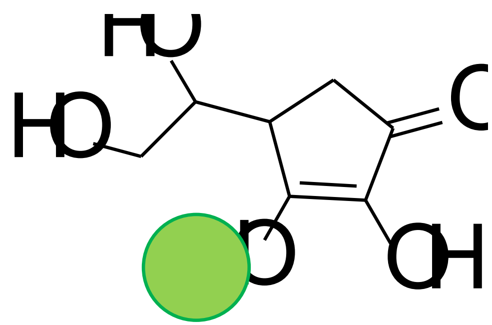
3. Vliv indukčního efektu



4,75 2,87 1,25 0,70

CH_3OH			
15,5	**16,0**	**17,1**	**19,2**

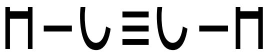




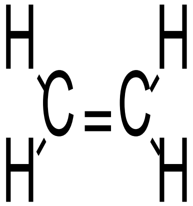
kyselina askorbová $pK_a = 4,2$

4. Vliv hybridizace

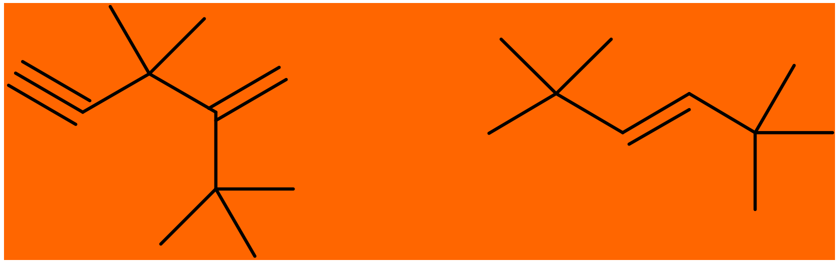
p*Ka*

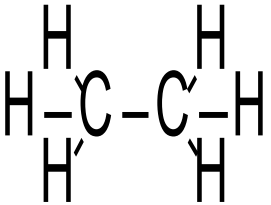


25



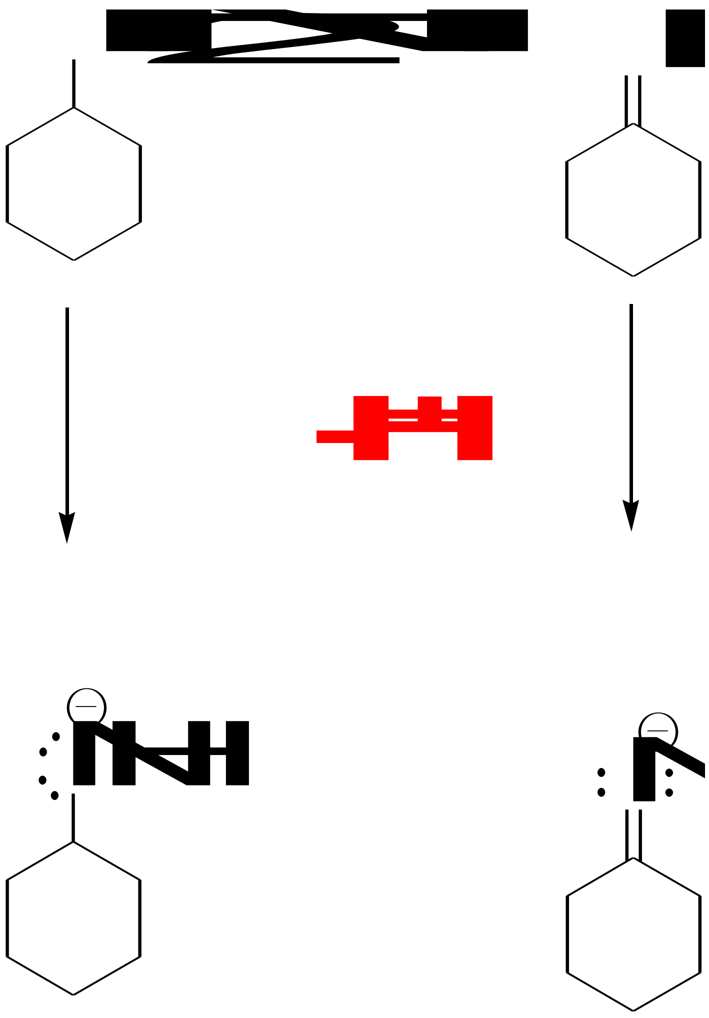
44





50

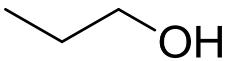
Která ze sloučenin je kyselejší, amin nebo imin?

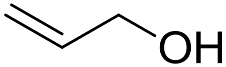


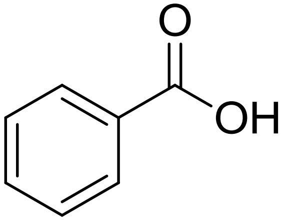
kyselejší

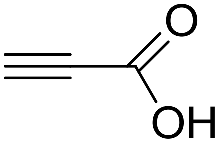
stabilnější

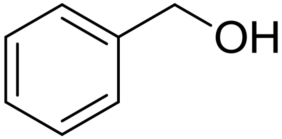
16,1 15,5 4,2 1,9

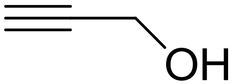


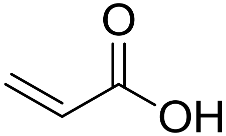


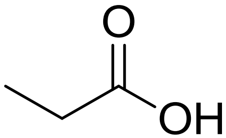




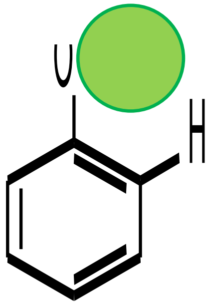
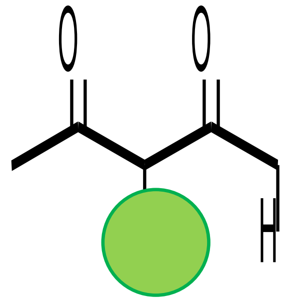
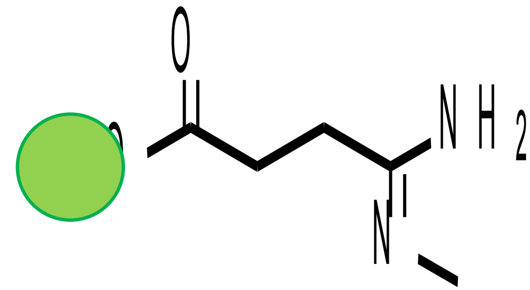
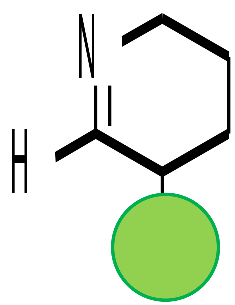
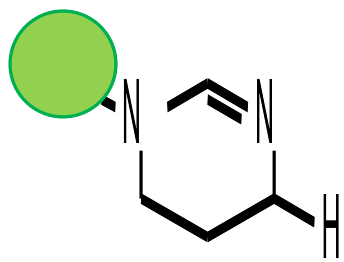
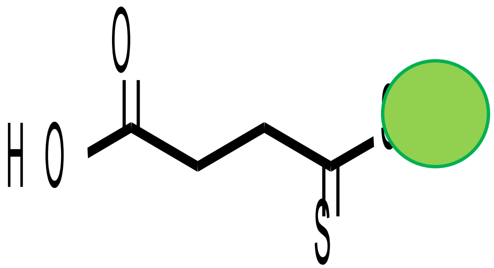
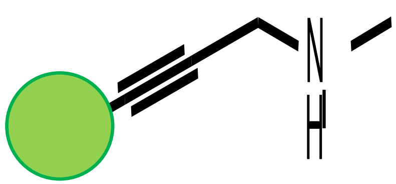
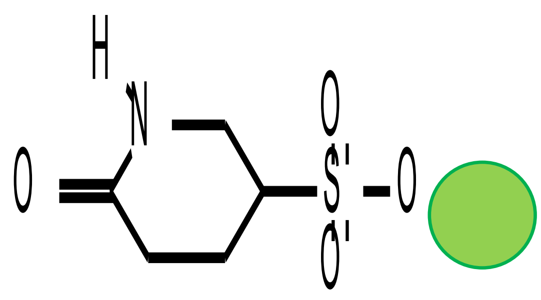
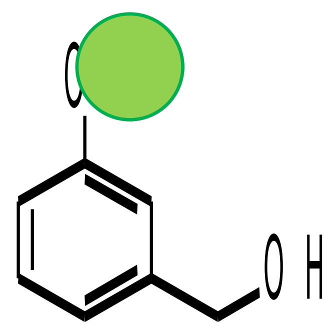




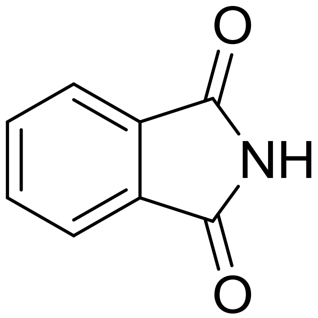


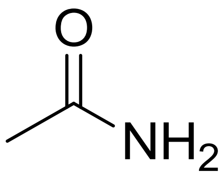


15,4 13,5 4,2 4,9

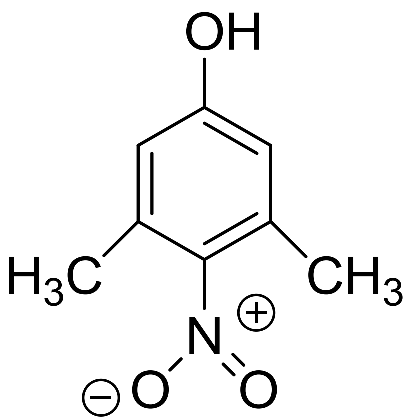
Která ze sloučenin je silnější kyselinou

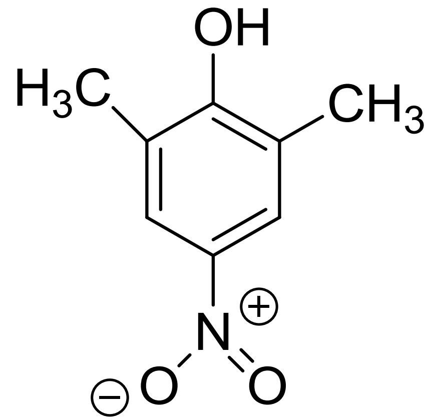




pK_A	8,3	17

Která ze sloučenin je silnější kyselinou



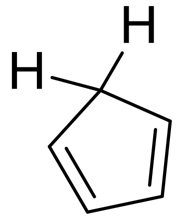


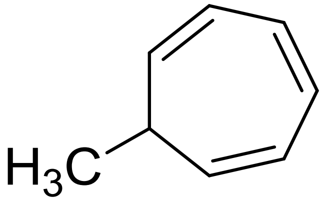
KYSELOST

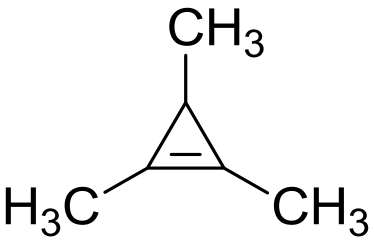
$<$

vychýlení z roviny, není dobrá konjugace, mezomerní efekt zeslaben

Která ze sloučenin je nejslabší a nejsilnější kyselinou

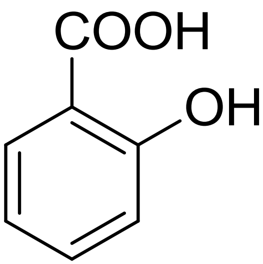


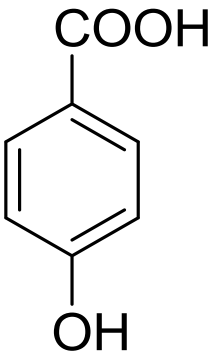




p*Ka*	15,5	36	62

Intramolekulární vodíková vazba





2,98

4,58

BAZICITA

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

$$K = \frac{[BH^+] \cdot [OH^-]}{[B] \cdot [H_2O]}$$

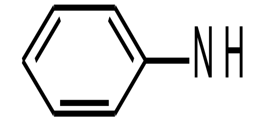
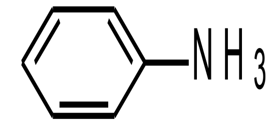
$$K \cdot [H_2O] = \frac{[BH^+] \cdot [OH^-]}{[B]} = K_B$$

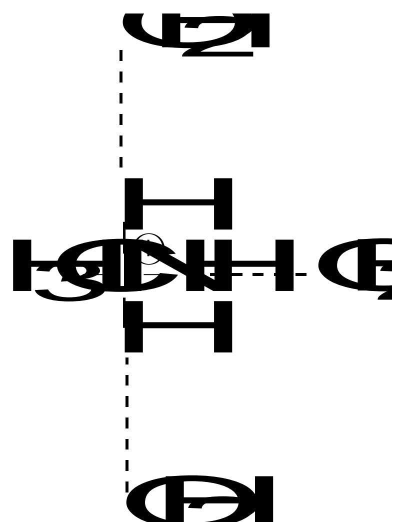
$$K_B = \frac{[BH^+] \cdot [OH^-]}{[B]}$$

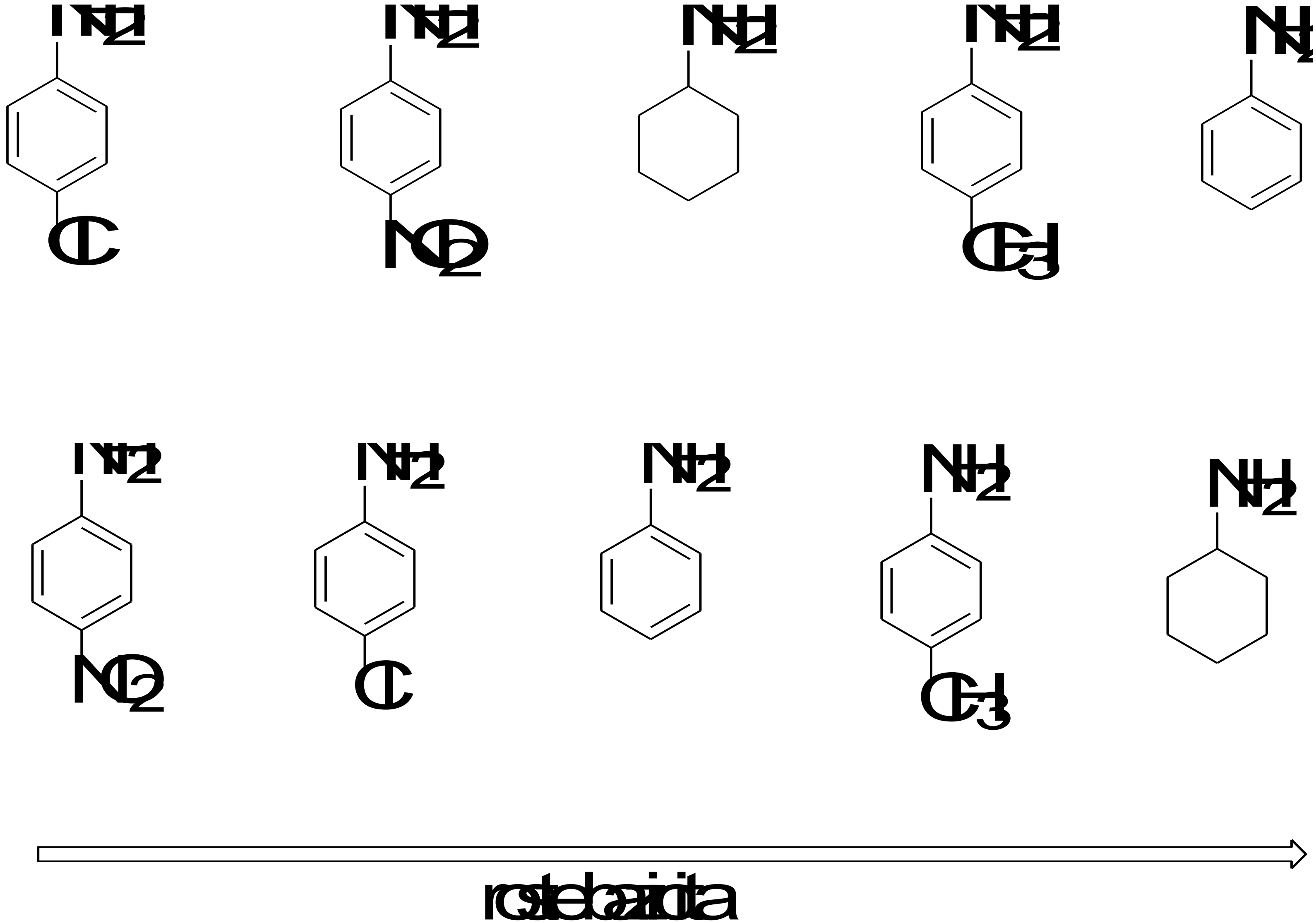
$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

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

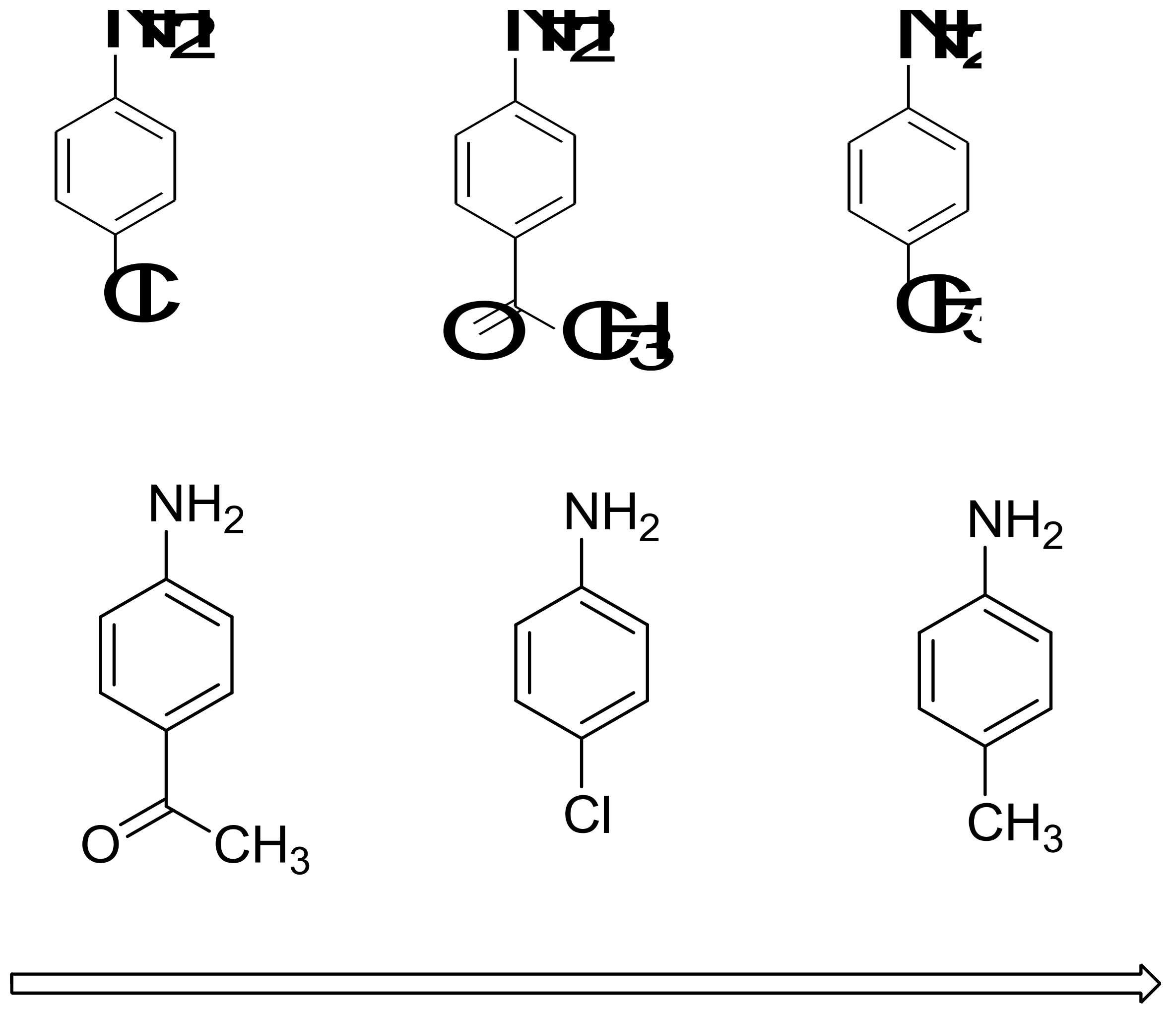
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	**p*K*$_B$**	4,75
$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$	**p*K*$_{AH}$**	9,25
$NH_3 + H_2O \rightleftharpoons NH_2^- + H_3O^+$	**p*K*$_A$**	35

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	
pK_{AH}	NH_4^+	$CH_3NH_3^+$	$(CH_3)_2NH_2^+$	$(CH_3)_3NH^+$	
					4,58





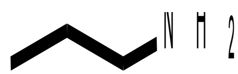
Seřaďte podle vzrůstající bazicity



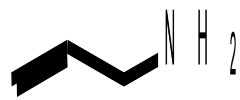
bazicita

Která ze sloučenin je nejsilnější bazí

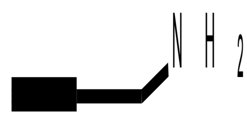
pKAH



10,7



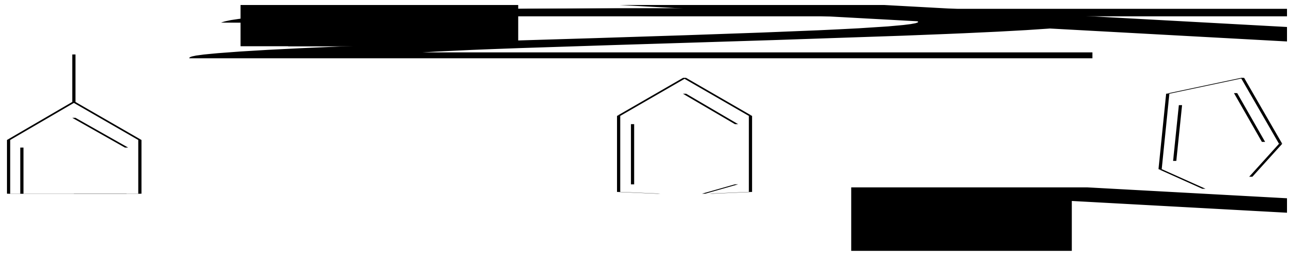
9,5

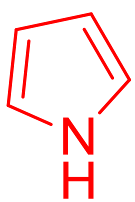


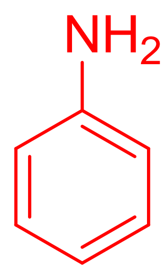
8,2

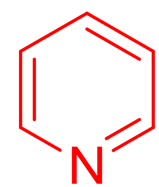
vliv hybridizace na sousedním uhlíku

Uvedené sloučeniny seřaďte podle vzrůstající bazicity



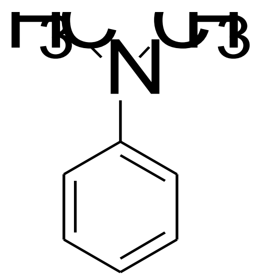


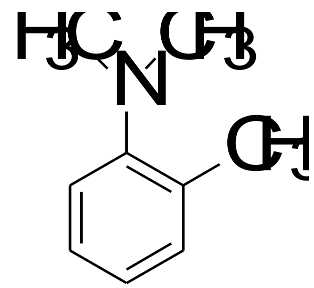




pK_{AH}	-3,8	4,63	5,25

Která ze sloučenin je silnější bazí

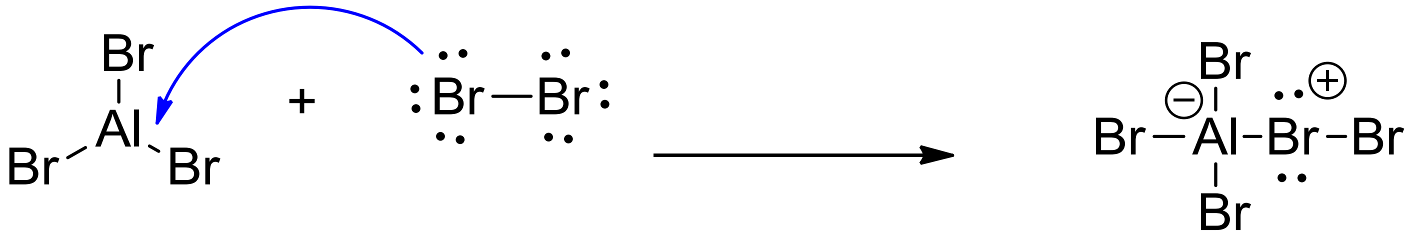


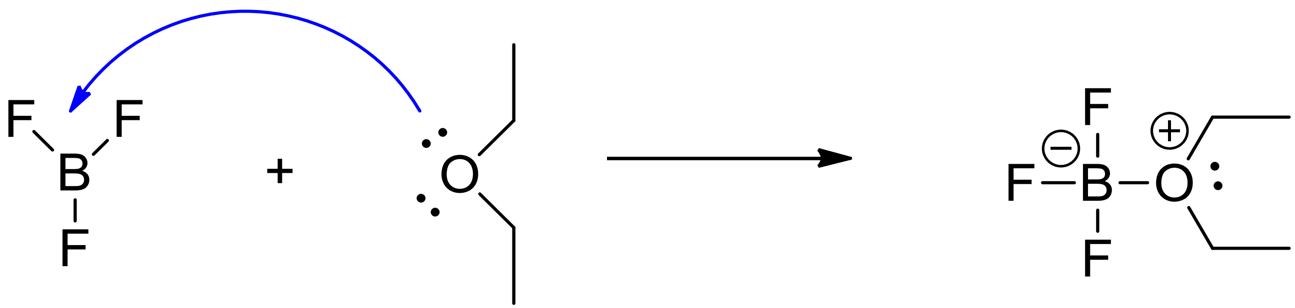


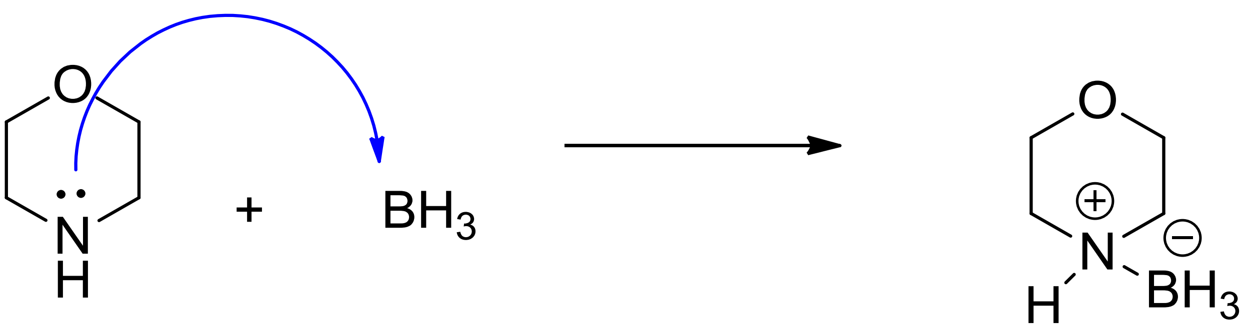
[redacted]

[redacted]

[redacted]





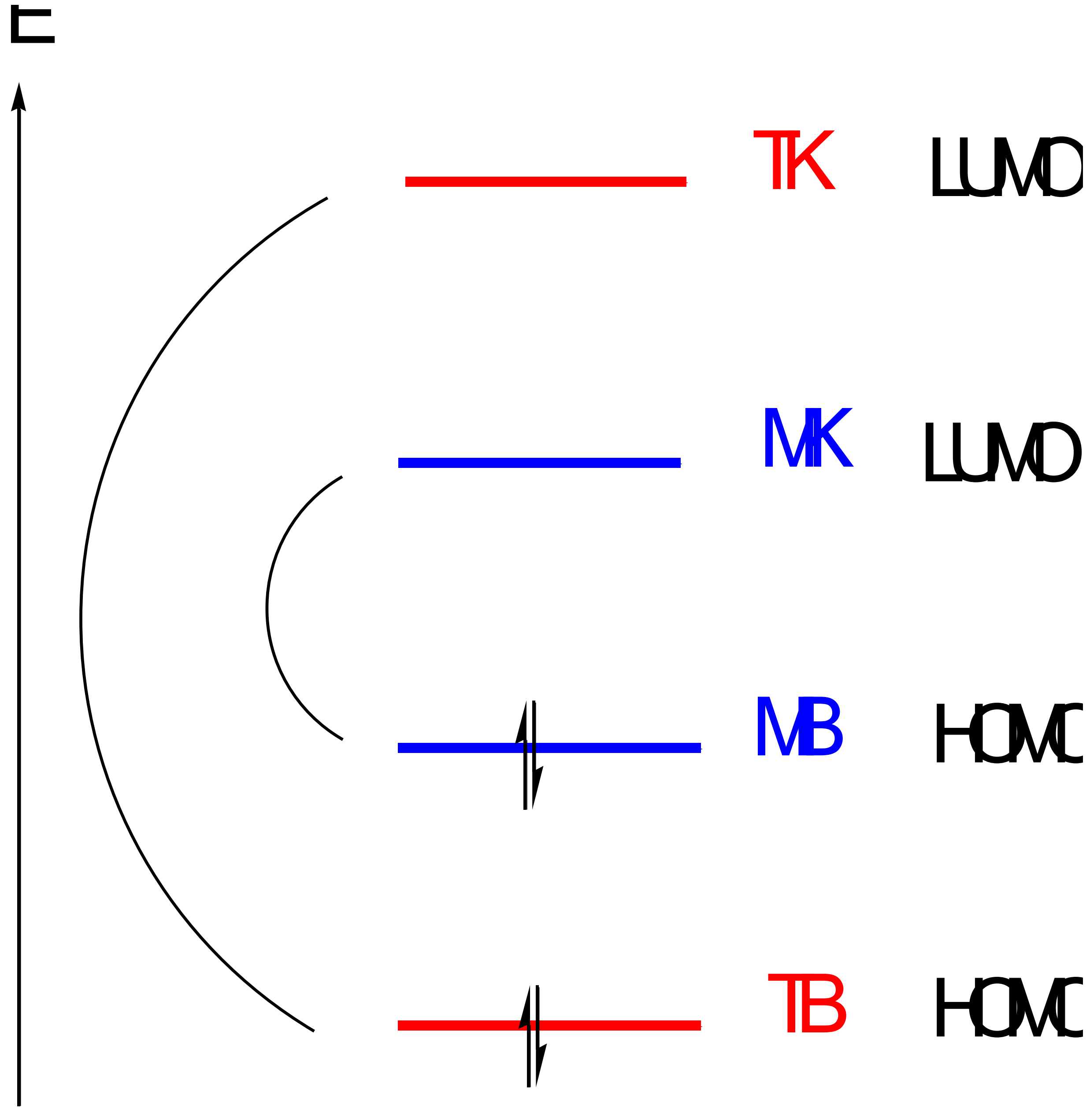


Pearsonova teorie HSAB

- Pearson postuluje ve své teorii, že každá látka sestává z bazické a kyselé části
- Tvrdé kyseliny reagují přednostně s tvrdými bázemi za vzniku stabilních komplexů a měkké kyseliny s měkkými bázemi
- Komplexy tvrdých kyselin s měkkými bázemi a měkkých kyselin s tvrdými bázemi jsou nestabilní
- Tvrdost a měkkost souvisí s polarizovatelností částic

  Měkké zásady obsahují atom snadno polarizovatelný či snadno oxidovatelný – reaktivita se koreluje s nukleofilitou

  Tvrdé zásady jsou látky s těžce oxidovatovatelnými atomy, obtížně polarizovatelnými – snadno reagují s protonem – korelují s bazicitou



E
TK
LUMO
MK
LUMO
MB
HOMO
TB
HOMO

Classification of Lewis Acids

Class (a)/Hard	Class (b)/Soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}	CH_3Hg^+
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}	Tl^{3+}, $Tl(CH_3)_3$, RH_3
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}, VO^{2+}	RS^+, RSe^+, RTe^+
UO_2^{2+}, $(CH_3)_2Sn^{2+}$	I^+, Br^+, HO^+, RO^+
$BeMe_2$, BF_3, BCl_3, $B(OR)_3$	I_2, Br_2, INC, etc.
$Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$	Trinitrobenzene, etc.
RPO_2^+,$ROPO_2^+$	Chloranil, quinones, etc.
RSO_2^+, $ROSO_2^+$, SO_3	Tetracyanoethylene, etc.
I^{7+}, I^{5+}, Cl^{7+}	O, Cl, Br, I, R_3C
R_3C^+, RCO^+, CO_2, NC^+	M^0 (metal atoms)
	Bulk metals
HX (hydrogen-bonding molelcules)	
Borderline	
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	
$B(CH_3)_3$, SO_2, NO^+	

Classification of Bases

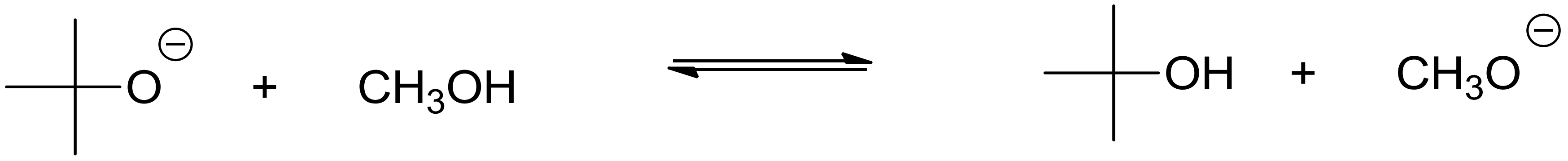
Hard	Soft
H_2O, OH^-, F^-	R_2S, RSH, RS^-
$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$
ROH, RO^-, R_2O	CN^-, RNC, CO
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6
	H^-, R^-

Borderline
$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2

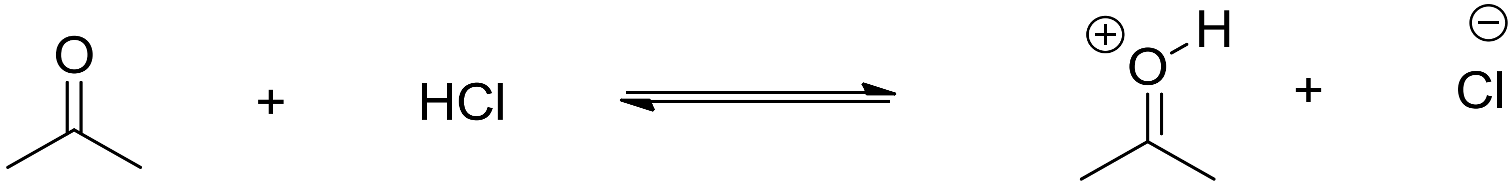
Kterým směrem bude posunutá rovnováha uvedené reakce

$$EtOH + NaOH \rightleftharpoons EtO^{\ominus} + H_2O$$

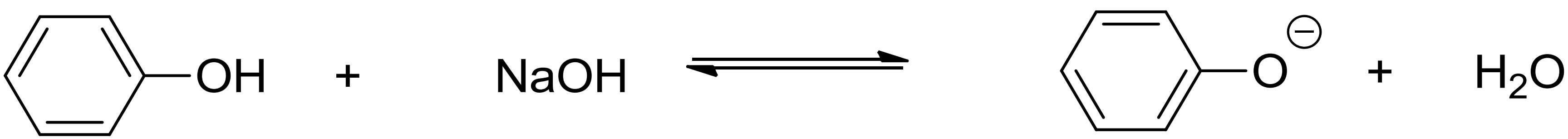
$$CH_3OH + NaNH_2 \rightleftharpoons CH_3O^{\ominus} + NH_3$$

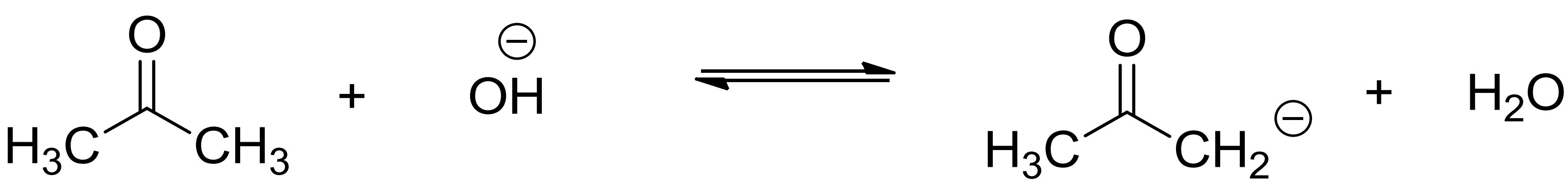


Kterým směrem bude posunutá rovnováha uvedené reakce



pK_A -7 -7,3

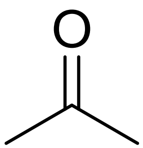




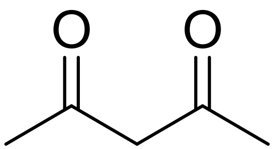
pK_A 19,3 15,7

Která z látek může svůj nejkyselejší vodíkový atom odštěpit působením $NaHCO_3$

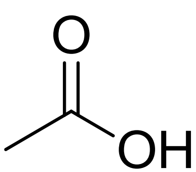
pK_A

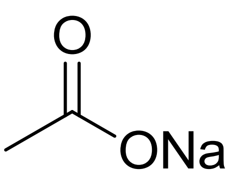


19,3

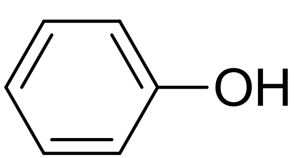


9



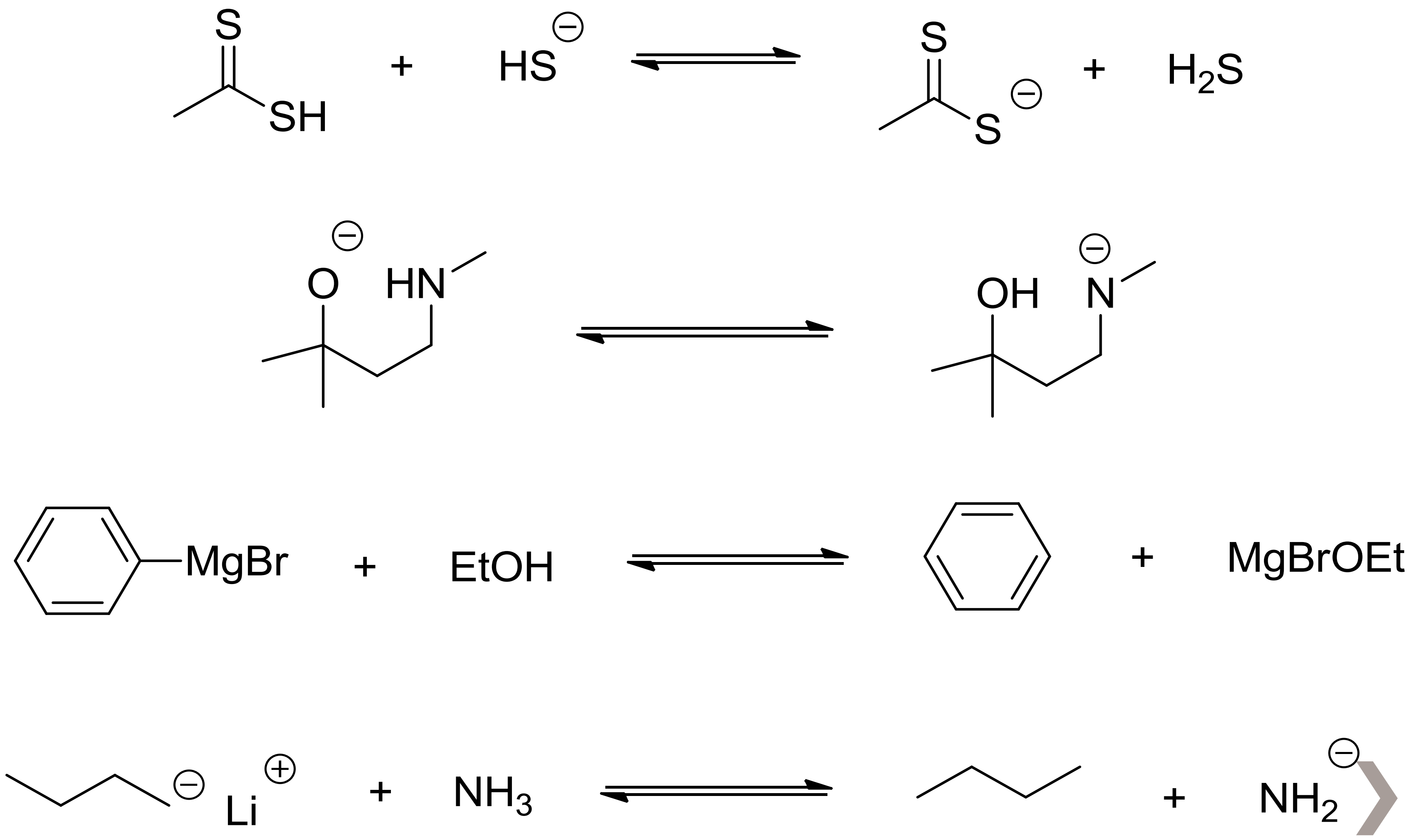
4,76 + $NaHCO_3$ →  + H_2CO_3

6,37



10

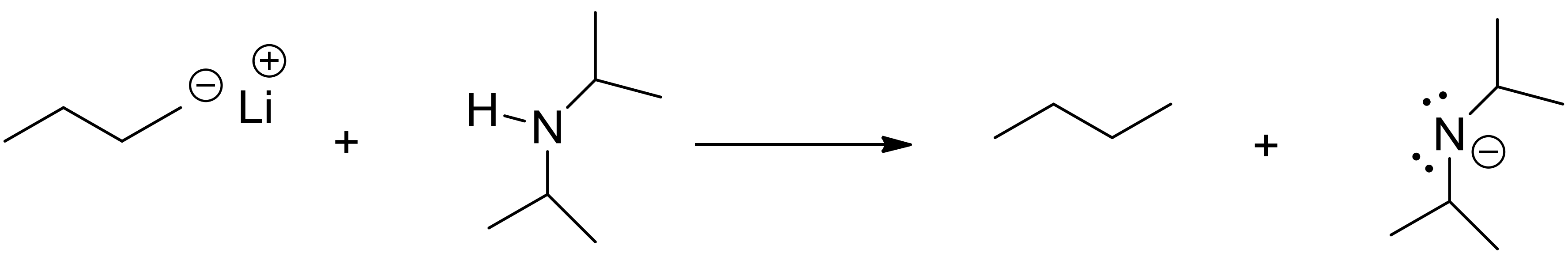
Kterým směrem bude posunutá rovnováha uvedené reakce



Báze silnější než OH⁻ nemohou být použité ve vodě

$$NH_2^- + H_2O \longrightarrow NH_3 + OH^-$$

p*K*$_A$ 15,7 35



p*K*$_A$ 40 50