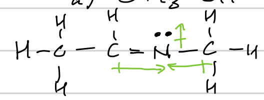
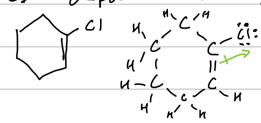
Ch2 HW - 2-29a, g, f part 2 and 3; 2-31a, d, j, i; 2-34; 2-35c, f; 2-36; 2-37; 2-42 g, h; 2-45; 2-48; 2-50 a, d, g; 2-52a, f; 2-56

2-29 a) $CH_3-CH=N-CH_3$



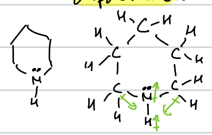
Yes dipole moment large

g)



Yes dipole moment moderate *why*

f)



Yes dipole moment moderate *not large?*

2-31) a) $(CH_3CH_2)_2NH$

This compound can H-bond with itself due to the δ^+ on Hydrogen and δ^- on Nitrogen. This also allows it to H-bond with water, increasing solubility.

d) $(CH_3CH_2CH_2)_2O$

The lone pair on the Oxygen allow it to H-bond with water, but no δ^+ on Hydrogen prevents H-bonding w/ itself. It will be soluble in water.

j)

can H-bond with water, but not itself. It is soluble.

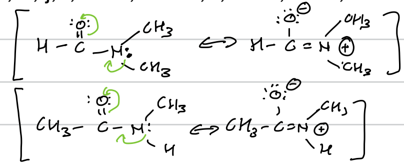
i) CH_3CH_2CHO

This can't H-bond with itself due to no δ^+ on the Hydrogen. This compound is an aldehyde so it ends with C(=O)-H. It can H-bond with water due to Oxygen lone pairs. This means it is soluble in water too.

2-34) a) Piperdine has a higher bp because it can H-bond with itself, while N-methylpyrrolidine has no H-bonding so it is easier and requires less energy to separate itself.

b) cyclopentanol has a higher bp than tetrahydropyran for a similar reason as (a). The OH H-bond is very strong and takes much more energy to separate molecules bonded this way. That also accounts for differences between the N-H molecule and O-H molecule.

2-34 c)



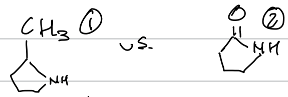
The nitrogen containing isomers have much higher bp differences because of the more linear structure. *why compared to amides?* These two are much more stable bc of resonance

Resonance forms → inc. stability → higher bp.

2-35 c) $CH_3CH_2CH_2CH_2CH_3$ (1) vs. $(CH_3)_2CHCH_2CH_3$ (2)

Compound 1 will have higher bp because it is a straight chain. So it has more surface area and thus stronger LDFs than compound 2.

f)



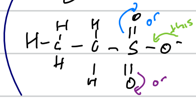
comp 1 < comp 2 bc it can H-bond with itself more effectively bc of the lone pairs on the oxygen.

2-36) All of the following compounds can react as acids. Without using a table of acidities, rank them in order of increasing acidity. Explain your ranking.

(a) $CH_3CH_2SO_3H$ (b) CH_3CH_2OH (c) CH_3CH_2COOH
(d) $CH_3CHClCOOH$ (e) $ClCH_2CH_2COOH$

b < c < e < d < a

for a



Resonance makes this conj. base super stable as illustrated roughly above.

c has resonance in its conj base but d and e are stabilized due to the inductive effect. d's Cl groups closer to -COOH than e, so it's more stabilized by

2-37) Rank the following species in order of increasing acidity. Explain your reasons for ordering them as you do.

~~HF~~ ~~NH_3~~ ~~H_2SO_4~~ CH_3OH CH_3COOH ~~H_3O^+~~ ~~H_2O~~

TABLE 2-2 RELATIVE STRENGTH OF SOME COMMON ORGANIC AND INORGANIC ACIDS AND THEIR CONJUGATE BASES

	Acid					Conjugate Base		K_a	pK_a
strong acids (stronger)	HCl hydrochloric acid	+ H_2O	⇌	H_3O^+	+	Cl^- chloride ion	weaker bases	1×10^7	−7
	H_3O^+ hydronium ion	+ H_2O	⇌	H_3O^+	+	H_2O water		55.6	−1.7
	HF hydrofluoric acid	+ H_2O	⇌	H_3O^+	+	F^- fluoride ion		6.8×10^{-4}	3.17
	H−C(=O)−OH formic acid	+ H_2O	⇌	H_3O^+	+	H−C(=O)−O^- formate ion		1.7×10^{-4}	3.76
	CH_3−C(=O)−OH acetic acid	+ H_2O	⇌	H_3O^+	+	CH_3−C(=O)−O^- acetate ion		1.8×10^{-5}	4.74
weak acids	H−C≡N: hydrocyanic acid	+ H_2O	⇌	H_3O^+	+	$^-$:C≡N: cyanide ion		6.0×10^{-10}	9.22
	$^+NH_4$ ammonium ion	+ H_2O	⇌	H_3O^+	+	$:NH_3$ ammonia		5.8×10^{-10}	9.24
	H_2O water	+ H_2O	⇌	H_3O^+	+	HO^- hydroxide ion		1.8×10^{-16}	15.7
	CH_3CH_2−OH ethyl alcohol	+ H_2O	⇌	H_3O^+	+	$CH_3CH_2O^-$ ethoxide ion		1.3×10^{-16}	15.9
very weak	NH_3 ammonia	+ H_2O	⇌	H_3O^+	+	$^-:\ddot{N}H_2$ amide ion		10^{-36}	36
not acidic (weaker)	CH_4 methane	+ H_2O	⇌	H_3O^+	+	$^-:CH_3$ methyl anion	stronger bases	$<10^{-50}$	50

A lower pKa correlates to a stronger acid, as it is the -log of Ka. Using that knowledge along with the table to the right to

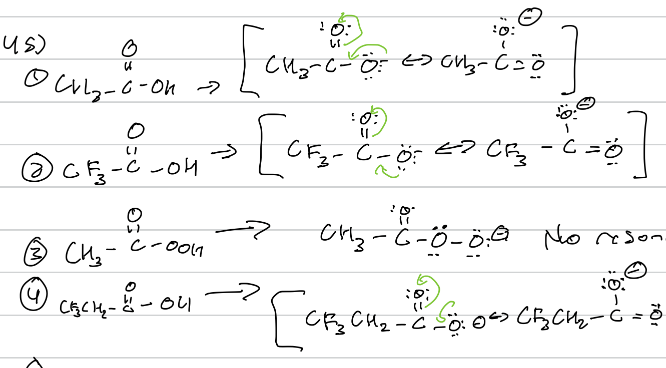
$NH_3 < H_2O < CH_3OH < CH_3COOH < HF < H_3O^+ < H_2SO_4$
36 15.7 15.5 4.74 3.17 −1.7

CH_3OH had to be looked up, but it is obvious that H_2SO_4 is the strongest acid

2-42 g) $HCOOH + CH_3O^- \rightleftharpoons HCOO^- + CH_3OH$
acid, Base, Conj base, conj acid

h) $^+NH_3CH_2COOH + 2\ ^-OH \rightleftharpoons NH_2CH_2COO^- + 2H_2O$
acid, base, Conj. base, Conj. acid

2-45)



(2) Inductive effect Stabilizes bc F is EN

(3) No resonance!! ... weak inductive

(4) weaker inductive effect as F is far

(5) $CH_3CH_2OH \rightarrow CH_3CH_2O^-$ no resonance!!

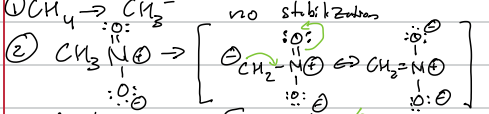
Rank conj. base stability: 2 > 4 ≥ 1 > 3 > 5
Rank acid strength: 2 > 4 > 1 > 3 > 5
most → least

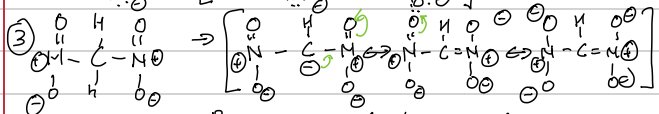
2-48) Consider the following compounds that vary from nearly nonacidic to strongly acidic. Draw the conjugate bases of these compounds, and explain why the acidity increases so dramatically with substitution by nitro groups.

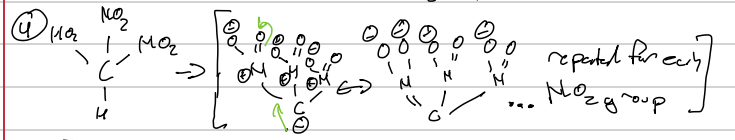
CH_4	CH_3NO_2	$CH_2(NO_2)_2$	$CH(NO_2)_3$
$pK_a \cong 50$	$pK_a = 10.2$	$pK_a = 3.6$	$pK_a = 0.17$
①	②	③	④

The NO_2 group is so strong because it opens the door to induction and strong resonance stabilization.

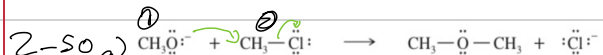
① $CH_4 \rightarrow CH_3^-$ no stabilization

② $CH_3NO_2 \rightarrow$  Resonance

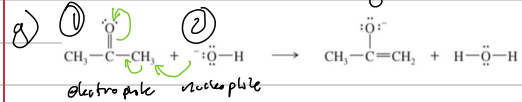
③  Resonance and strong induction

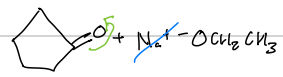
④  repeated for each NO_2 group

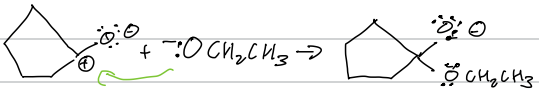
Tons of resonance stabilization and induction → most stabilization

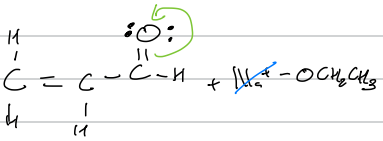
2-50 a) 
nucleophile electrophile

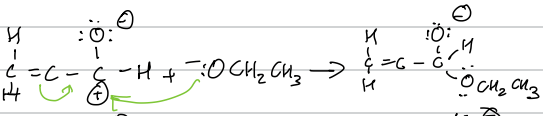
d) 
2 e⁻ transfers here
nucleophile electrophile

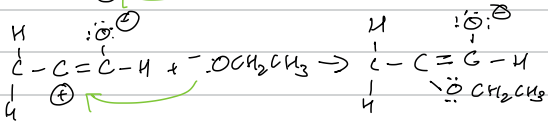
g) 
2 e⁻ transfer again
electrophile nucleophile

2-52a) 

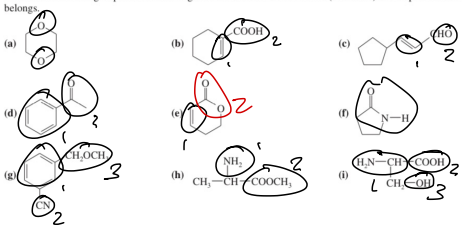


f) 

1) 

2) 

2-56) Circle the functional groups in the following structures. State to which class (or classes) of compounds the structure belongs.



a) both ethers

b) 1 = alkene, 2 = carboxylic acid

c) 1 = alkene, 2 = aldehyde (are these always aldehydes?)

d) 1 = benzene/phenol/aromatic, 2 = ketone

e) 1 = alkene 2 = ester

f) amide

g) 1 = aromatic, 2 = nitrile, 3 = ether

h) 1 = amine, 2 = ester

i) 1 = amine, 2 = carboxylic acid 3 = alcohol