KEY

STRUCTURE ACIDITY / BASICITY PREDICTIONS

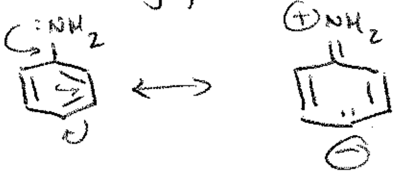
ACIDS

HCl $\longrightarrow$ $H^+ + Cl^-$, strongest acid, H^+ must be stabilized by H_2O

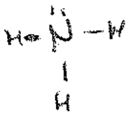
$[C_6H_5NH]Cl$ $\longrightarrow$

$+ Cl^-$

$\longrightarrow$ look at conjugate base, lone pair is stabilized by resonance



$NH_4Cl \longrightarrow NH_4^+ + Cl^-$ $\longrightarrow$ look at CB



$[Et_3NH]Cl \longrightarrow Et_3NH^{\oplus}\ Cl^-$ $\longrightarrow$ look at CB

neither base is resonance stabilized, so both are strong bases with weak acids

hard to predict which acid is weaker w/o more info.

Ranking based on pKa

H^+	< 0	most acidic
$C_6H_5NH_3^+$	4.6	
NH_4^+	9.2	
Et_3NH^+	10.6	least acidic

BASES

$KOI \longrightarrow K^+ + \overset{\ominus}{:}\ddot{\underset{..}{O}}-\overset{\leftarrow\!+}{\ddot{\underset{..}{I}}}:$

ΔEN = 3.5 − 2.2
= 1.3

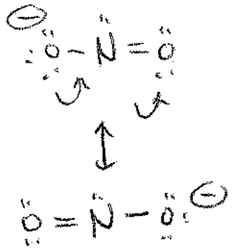
$NaCN \longrightarrow Na^+ + \overset{\ominus}{:}\overset{+\!\!\rightarrow}{C\equiv N}:$

ΔEN = 3.0 − 2.5
= 0.5

$KOCl \longrightarrow K^+ + \overset{\ominus}{:}\ddot{\underset{..}{O}}-\overset{\leftarrow\!+}{\ddot{\underset{..}{Cl}}}:$

ΔEN = 3.5 − 2.8
= 0.7

$NaNO_2 \longrightarrow Na^+$



IT'S HARDER TO PLACE CN^- SINCE MULTIPLE FACTORS ARE AT PLAY

↓

carbon has a -1 formal charge (not stable) but C is sp hybridized

The greater EN of Cl vs that of I leads to a smaller inductive effect so the charge on Oxygen is more stable in ^-OCl.

most stable base (weakest) due to resonance stabilization charge is delocalized over 3 atoms.

Ranking based on pK_b

OI^-	3.5
CN^-	4.8
OCl^-	6.5
NO_2^-	10.6

a) lowest pH : strongest acid : HCl
weakest base : $NaNO_2$

$$\underset{SA}{HCl_{(aq)}} + \underset{WB}{NaNO_{2\,(aq)}} \longrightarrow \underbrace{\underset{Salt}{NaCl_{(aq)}} + \underset{WA}{HNO_{2\,(aq)}}}_{}$$

STABLE PRODUCTS

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 4\times10^{-4} \longleftarrow$$

{ HNO_2 is the dominant species after neutralization of $NaNO_2$

$$4\times10^{-4} = \frac{x^2}{0.10 - x} \implies x^2 \approx 4\times10^{-5}$$

$$x \approx 6._3\times10^{-3}$$

$$pH = -\log(6._3\times10^{-3}) = 2.2$$

b) highest pH: weakest acid : $[Et_3NH]^+Cl^{\ominus}$
strongest base : $K^+\ IO^{\ominus}$

$$[Et_3NH]^+ + IO^- \rightleftharpoons HOI + Et_3N$$

$K_a = 2._5\times10^{-11}$ $K_b = 3._2\times10^{-4}$ $K_a = 3._1\times10^{-11}$ $K_b = 4\times10^{-4}$

NOTICE FIRST THAT THE REACTANTS ARE ON THE WEAK SIDE.
THEN COMPARE K_a to K_b. Since $K_b > K_a$ the solution will be basic.
NOW WRITE ALL THE IMPORTANT EQUILIBRIA

$$[Et_3NH]^+ + \cancel{H_2O} \rightleftharpoons Et_3N + \cancel{H_3O^+} \qquad K_a = 2.5\times10^{-11}$$

$$IO^- \cancel{+H_2O} \rightleftharpoons HOI + \cancel{OH^-} \qquad K_b = 3._2\times10^{-4}$$

$K_a\times K_b = 8\times10^{-15}$

$$\cancel{H_3O^+} + \cancel{OH^-} \rightleftharpoons \cancel{H_2O} + \cancel{H_2O} \qquad 1/K_w = 1.0\times10^{14}$$

THIS HAS TO BE INCLUDED SINCE IT COMPETES WITH $K_a + K_b$

$$[Et_3NH]^+ + IO^- \rightleftharpoons Et_3N + HOI$$

$$K' = (2._5\times3._2\times1.0)\times10^{(-11-4+14)}$$

$$\boxed{K' = 8\times10^{-1}}$$

More simply, since you know the solution will be basic ← K' is just the ratio of the K_b of weaker base to that of the stronger base

$$= \frac{K_{a\,[Et_3NH]^+}}{K_{a\,HOI}} = \boxed{\frac{K_{b\,IO^-}}{K_{b\,Et_3N}}}$$

b) Continued . . .

$$[Et_3NH]^+ + IO^- \rightleftharpoons HOI + Et_3N \qquad K' = 0.8$$

i	0.10	0.10	0	0
c	$-x$	$-x$	$+x$	$+x$
e	$0.10-x$	$0.10-x$	x	x

$$\frac{x^2}{(0.10-x)^2} = 0.8 \Rightarrow \frac{x}{0.10-x} = 0.8$$

$$x = 0.08 - 0.8x$$

$$1.8x = 0.08$$

$$x = 0.04_4 = [HOI] = [Et_3N] \quad , \quad 0.10-x = 0.05_6 = [IO^-] = [Et_3NH]^+$$

Now, one can solve

for pH using K_a or pOH using K_b

HIO

$$K_a = \frac{[H_3O^+][IO^-]}{[HOI]}$$

$$3._1\times10^{-11} = \frac{[H_3O^+][0.05_6]}{[0.04_4]}$$

$$[H_3O^+] = \underline{2}.4\times10^{-11}$$

$$pH = 10.6$$

✓

IO^-

$$K_b = \frac{[OH^-][HIO]}{[IO^-]}$$

$$\underline{3}.2\times10^{-4} = \frac{[OH^-][0.04_4]}{[0.05_6]}$$

$$[OH^-] = 4._1\times10^{-4}$$

$$pOH = 3.4$$

$$pH = 10.6$$

NOTE,

THE IO^- is stronger as a base than $[Et_3NH]^+$ as an acid, so one uses the IO^- and K_b or HIO and K_a to find pH not Et_3NH^+ or Et_3N

c) pH closest to 7 $\quad pK_a \approx pK_b$

$$\begin{array}{cc} pK_a & pK_b \\ \downarrow & \downarrow \\ 10.6 & 10.6 \\ \text{for} & \text{for} \\ [Et_3NH]^+ & NaNO_2 \end{array}$$

$$[Et_3NH]^+ + \cancel{H_2O} \rightleftharpoons Et_3N + \cancel{H_3O^+} \qquad K_a = 2._5 \times 10^{-11}$$

$$NO_2^- + \cancel{H_2O} \rightleftharpoons HNO_2 + \cancel{OH^-} \qquad K_b = 2._5 \times 10^{-11}$$

$$\cancel{H_3O^+} + \cancel{OH^-} \rightleftharpoons \cancel{H_2O} + \cancel{H_2O} \qquad 1/K_w = 1.0 \times 10^{14}$$

$$Et_3NH^+ + NO_2^- \rightleftharpoons HNO_2 + Et_3N \qquad K' = \underline{6}.2 \times 10^{-8}$$

equil. $0.10 - x \quad 0.10 - x \quad x \quad x$

such a small K' that pH will be close to 7

$$\frac{x^2}{(0.10-x)^2} = 6._2 \times 10^{-8}$$

$$x \approx \sqrt{6._2 \times 10^{-9}}$$

$$x = 7._8 \times 10^{-5}$$

$$\underset{Et_3NH^+}{K_a} = 2._5 \times 10^{-11} = \frac{[H_3O^+]\overset{[Et_3N]}{(7._8 \times 10^{-5})}}{\underset{[Et_3NH]^+}{(0.10 - 7._8 \times 10^{-5})}}$$

$$[H_3O^+] = \underline{3}.2 \times 10^{-8}$$

pH = 7.5