Workshop 4

Answers

4) Lewis Acid/base reaction

a) Formal charge = number of valence e− - neutral - (all unshared e− + 1/2 shared e−)
The equilibrium favors the direction that gives the weaker acid and the weaker base. Eq. will favor formation of an acid with a pKa value higher than 4.7.

The equilibrium favors the reaction of the stronger acid and the stronger base to give the weaker acid and the weaker base. In this case the acid formed is stronger (↓ pKa), so it's not favoured.
d) \[
\text{CH}_3 - C \equiv C - \text{H} + \overset{\text{N}}{\text{H}} - \text{H} \rightarrow \text{CH}_3 - C \equiv C : - + \overset{\text{N}}{\text{H}}_3
\]
pK_a = 24  
acid  
base  

The eqn. favours the formation of the weaker acid ( \( \uparrow \) pK_a) 
so it goes in the direction \( \rightarrow \) 

Typical reaction for terminal alkenes

e) \[
\text{CH}_3 - \text{CH}_3
\]

\[
\text{CH}_3 - C - \text{H} + \overset{\text{N}}{\text{H}} - \text{H} \rightarrow \text{CH}_3 - \text{CH}_2 - + \overset{\text{N}}{\text{H}} - \text{H}
\]
pK_a 50  
acid  
base  

In this case the reaction won't proceed as the acid formed is stronger than the starting acid (lower pK_a)
2) \[ \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \] Acid + water →

We can define the equilibrium expression

\[
\text{Keq} = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad \text{Keq = constant of the equilibrium}
\]

Because water is the solvent for this reaction and its concentration changes very little when \( \text{HA} \) is added to it, we can treat the concentration of \( \text{H}_2\text{O} \) as a constant equal to 5000 g/L or \( \approx 55.6 \text{ mol/L} \).

We can then combine these two constants (\( \text{Keq} \) and the [\( \text{H}_2\text{O} \)]) to define a new constant called an acid dissociation constant \( \text{Ka} \).

\[ \text{Ka} = \text{Keq} \times [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}]} \]

Because dissociation constants for most acids, including organic acids, are numbers with negative exponents, acid strengths are often expressed as

\[ \text{pKa} = -\log_{10} \text{Ka} \]

b) \[ \text{NH}_4^+ \text{Cl}^- \rightarrow \text{NH}_4^+ + \text{Cl}^- \rightleftharpoons \frac{1}{1} \text{H}_2\text{O} \]

\[
\text{NH}_3 + \text{H}_3\text{O}^+ \]

\[ \text{Ka} = \frac{[\text{H}_3\text{O}^+] [\text{NH}_3]}{[\text{NH}_4^+] \text{Cl}^-} \]
d) \[ \Delta G^0 = -RT \ln K_{eq} \]

\[ \ln K_{eq} = -\frac{\Delta G^0}{RT} \]

- If \( \Delta G^0 > 0 \); the position of equilibrium favors reactants
- If \( \Delta G^0 < 0 \); the position of equilibrium favors products

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e) \[ HA + B^- \leftrightarrow BH^+ + A^- \]

\[ K_{eq} = \frac{[BH^+][A^-]}{[HA][B^-]} \]

1) \[ HA + H_2O \rightarrow H_3O^+ + A^- \quad K_a \quad K_b \]
2) \[ B^- + H_2O \rightarrow BH^+ + OH^- \quad K_a \quad K_b \]
3) \[ H_2O \rightarrow H_3O^+ + OH^- \quad K_b = K_w \quad \text{hydrolysis} \]

\[ K_{eq} = \frac{[BH^+][OH^-]}{[HA][OH^-]} = \frac{K_a}{K_b} \quad \frac{K_b}{[H_3O^+][A^-]} = \frac{K_a}{[OH^-]} \]

\[ K_{eq} = \frac{K_b K_a}{K_w} \]

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f) "The stronger base wins the protons"

The eq. favors reaction of the stronger acid and the stronger base to give weaker acid and base.

The base will abstract a proton from a Brønsted-Lowry acid to form a covalent bond with its lone pair of e-.
- "The weaker acid predominates"
  The eq. favors reaction of the stronger acid and the stronger base to give weaker acid and base.
- "Proton affinity tracks with pKa"
The smaller the value of pKa the stronger the acid is and the easier it will give protons away. The higher the value of pKa the weaker the acid will be and the more affinity it will have for protons.

\[ \begin{align*}
\text{CH}_3 - C = O & \quad + \quad \text{HO - C = O} \\
pKa = 4.7
\end{align*} \]

\[ \begin{align*}
\text{CH}_3 - C = O & \quad + \quad \text{HO - C = O} \\
\text{pKa} = 6.4
\end{align*} \]

b) \[ \begin{align*}
\text{H - CH}_2 - C - \text{CH}_3 & \quad + \quad \text{HO - S} \\
pKa = 20
\end{align*} \]

\[ \begin{align*}
\text{CH}_3 - C = \text{CH}_3 & \quad + \quad \text{HO - S} \\
pKa = 1.99
\end{align*} \]

It will react

pKa of resulting acid is higher
c) 
\[
\text{base} \quad \text{pK}_a = 9.25
\]
\[\text{acid} \quad \text{pK}_a = 15.7\]

\[\text{base} \quad \text{acid}\]

\[\text{adduct}\]

b. choose reactants

1) \((\text{CH}_3)_3\text{B} + \text{NC(CH}_3)_3\text{b} \rightarrow (\text{CH}_3)_3\text{B}^- + \text{N}^+ (\text{CH}_3)_3\]

2) \((\text{CH}_3)_2\text{C}=\text{O}^- + \text{H}_2\text{O}\rightarrow \text{SO}_2\text{OH} \rightarrow (\text{CH}_3)_2\text{C}=\text{O}^- \text{H}^+ + \text{SO}_2\text{OH}\]

3) \(\text{CH}_3^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{S}^- \text{CH}_3 + \text{Br}^-\)
5) 

a) \[ \text{CH}_3\text{C} = \text{C} - \text{CH}_3 \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{CCH}_3 \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{CH}_2\text{CCH}_3 \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{CCH}_3 \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{CH}_2\text{CCH}_3 \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_3 \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_3 \]

b) \[ \text{CH}_3\text{C} = \text{C} - \text{CH}_3 \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_3 \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \]

c) \[ \text{CH}_3\text{C} = \text{C} - \text{CH}_3 \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
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\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \]

d) \[ \text{CH}_3\text{C} = \text{C} - \text{CH}_3 \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{CH}_3\text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
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\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \] \\
\[ \text{H} \text{C} = \text{C} - \text{CH}_2\text{Br} \]

6) 

2) or

b) 4 chiral centers
There are \[ 2^4 = 16 \] stereoisomers possible

c) 3 rings, 4 double bonds \( \text{C} = \text{C}, \text{C} = \text{O} \)

\[ H_0 = 7 \]
P.E. of reactants ~ 16

\[
pK_a \text{ of } H_2O \text{ is } \sim 16 \quad (15.7)
\]

\[
\Delta H = 0 \quad \text{pK}_a \text{ units}
\]

\[
K_{eq} = 10^{-\Delta H}
\]

\[
K_{eq} = 10^{0} = 1
\]

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P.E. of products ~ 16

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P.E. of reactants ~ 16

\[
pK_a \text{ of F-H is } 3.2, \quad pK_a \text{ of } H_2O \text{ is } \sim 16 \quad (15.7)
\]

\[
\Delta H = \sim 13 \quad \text{pK}_a \text{ units}
\]

\[
K_{eq} = 10^{-\Delta H}
\]

\[
K_{eq} = 10^{13} = \text{very large number}
\]
ChemActivity 8: Acid-Base Reactions

Exercise Solutions

1. The higher the pKa of an acid the weaker the acid. The lower the pKa of an acid the stronger the acid.

2. For a given base, the higher the pKa of its conjugate acid, the stronger the base. For a given base, the lower the pKa of its conjugate acid, the weaker the base.

3. According to the charge effect they should be about the same V.E. But in Model 3 it says NH₃ is the stronger base.

4. pKa of F-H is 3.2, pKa of H₂O is 15.7

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ΔH = +13 pKa units

Kₑq = 10⁻¹³ = very small number
5. Reactivity is often equated with high potential energy, but they are not the same! A species is reactive if it is likely to move to a lower potential energy state. High potential energy species are often reactive because, like a ball at the top of a hill, there is opportunity to go DOWN. A low potential energy species can be reactive if it can easily be converted into a lower potential energy species, or if it can lower the potential energy of a species it reacts with. A strong acid does both. It easily gives up a proton (recall that a pKa of zero means it takes almost no energy to remove the proton). And in giving a proton to a base, it often dramatically lowers the potential energy of that base.