No Analytical Crib

4-29-06

Written by Professor Bakker

No Biochemistry Crib

4-29-06

Written by Professor Davidson

Answers INORGANIC CUME
April 29, 2006

(30pts) 1. (a) Derive rate expression if Cr(V) is a steady-state species:

$$\frac{d[Cr(V)]}{dt} = k_1[Cr(VI)][Fe(phen)_3^{2+}] - k_{-1}[Cr(V)][Fe(phen)_3^{3+}] - k_2[Cr(V)][Fe(phen)_3^{2+}] = 0$$

so

$$[Cr(V)] = \frac{k_1[Cr(VI)][Fe(phen)_3^{2+}]}{k_{-1}[Fe(phen)_3^{3+}] + k_2[Fe(phen)_3^{2+}]}$$

$$\frac{d[Fe(phen)_3^{3+}]}{dt} = 3k_2[Cr(V)][Fe(phen)_3^{2+}]$$

$$-\frac{d[Fe(phen)_3^{2+}]}{dt} = \frac{3k_2k_1[Cr(VI)][Fe(phen)_3^{2+}]^2}{k_{-1}[Fe(phen)_3^{3+}] + k_2[Fe(phen)_3^{2+}]}$$

(b) The steady-state approximation means that the concentration of Cr(V) is negligible during the reaction so that the approximation $\frac{d[Cr(V)]}{dt} = 0$ is valid.

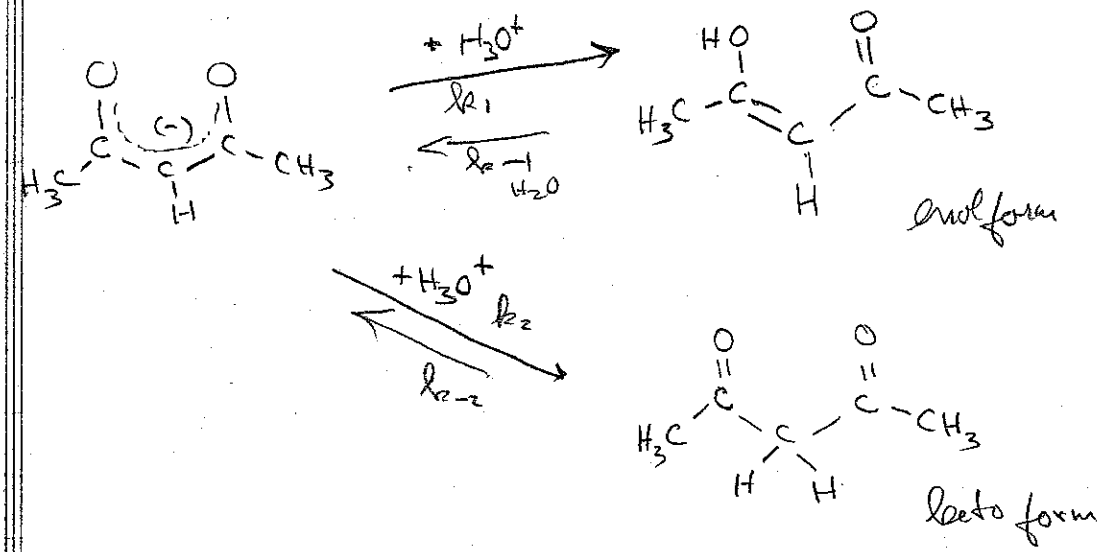
Note that the [Cr(IV)] also is negligible because rx 3 is fast and it is rapidly converted to Cr(III).

(c) The overall reaction is:

$$Cr(VI) + 3\,Fe(phen)_3^{2+} \longrightarrow Cr(III) + 3\,Fe(phen)_3^{3+}$$

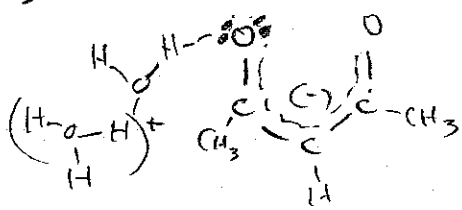
Hence, the factor of 3 in the rate expression.

(40 pts) 2. (a) Reactions of H_3O^+ with acac$^-$.



(1) Two possible products are the enol and keto forms of acetylacetone as shown.

(2) The reaction to give the enol form is faster, because hydrogen bonding to the enolic oxygen from water and H_3O^+ provides an excellent path for proton transfer. The electron-pairs on the oxygen can H-bond to water and to H_3O^+ to give a facile path for H^+ transfer



(3) The keto form is the more stable product with two hydrogen atoms bound to the middle carbon. The only reaction pathway from the enol to the keto form is via the reverse rx k_{-1} path followed by the k_2 path.

2(a) continued

$$[\text{enol form}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (acac^-) + H_3O^+$$

$$(acac^-) + H_3O^+ \xrightarrow{k_2} \text{keto form}$$

Once H_3O^+ converts $acac^-$ to the enol form, only trace levels of $acac^-$ are left (so it is a steady-state species) and

$$\frac{d[\text{keto}]}{dt} = k_2[H_3O^+][acac^-]$$

SSA in $[acac^-]$ gives $[acac^-]_{ss} = \dfrac{k_{-1}[\text{enol}]}{(k_{-1}+k_2)[H^+]}$

$$\frac{d[\text{keto}]}{dt} = k_2[H^+][acac^-]_{ss} = \frac{k_2 k_{-1}[\text{enol}]}{k_{-1}+k_2}$$

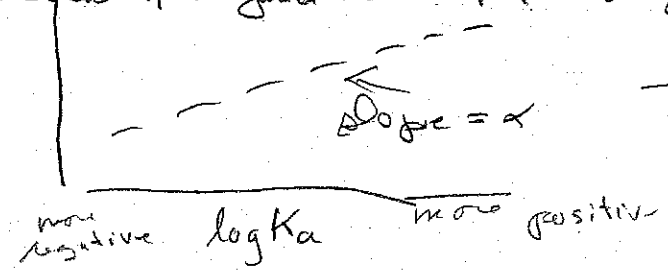
2(b) In general-acid-assisted reactions, the stronger the acid the faster the proton-transfer reaction.

Expected correlation for acids HA with various K_a values is the Brønsted relationship

$$k_{HA} = G_A K_a^{\alpha} \quad \text{or} \quad \log k_{HA} = \log G_A + \alpha \log K_a$$

Expected correlation

The greater the acidity the faster the H^+ transfer; range of slopes > 0 and < 1

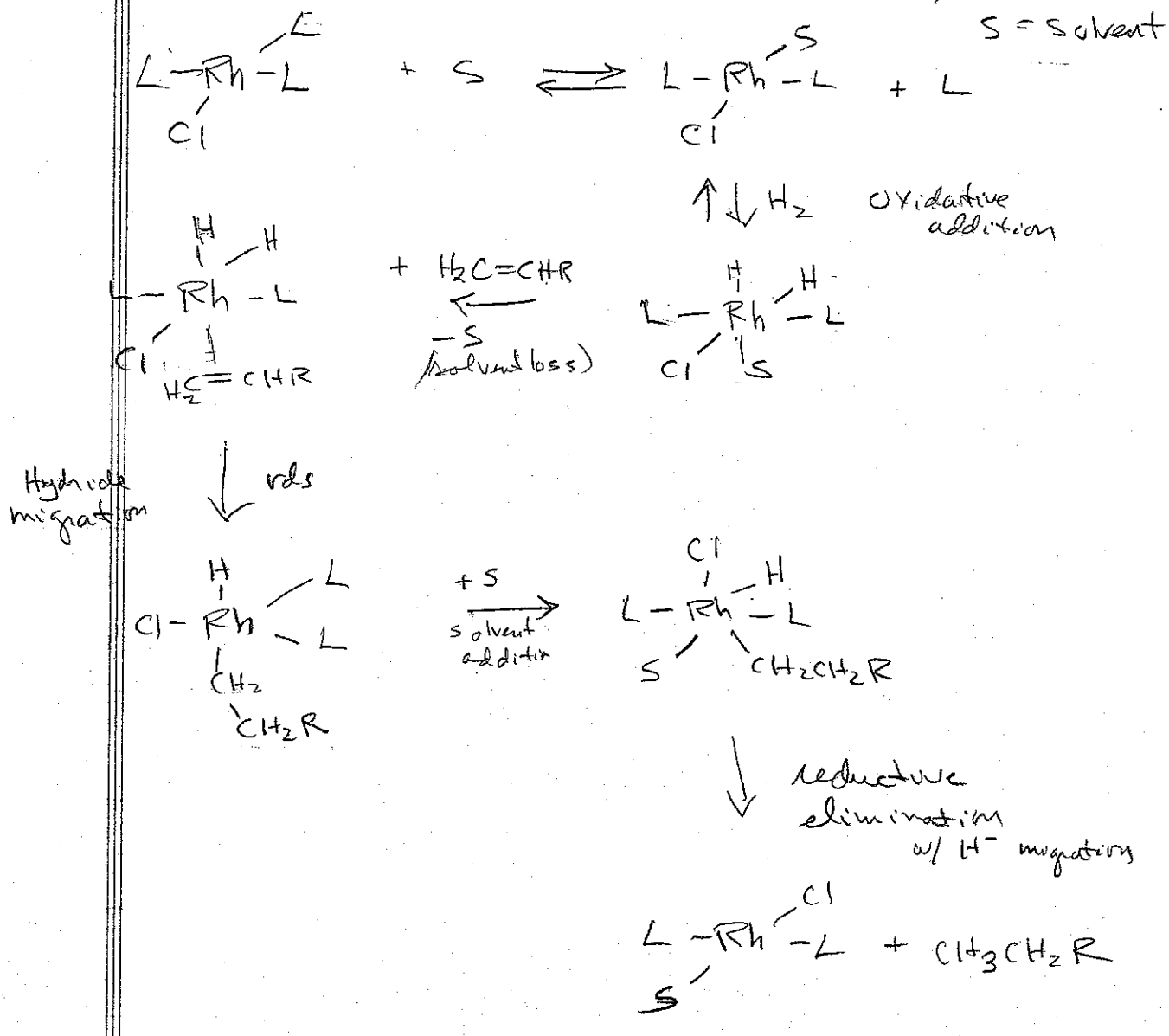


INORCHEM April 29, 2006

(30pts) 3. Alkene ($H_2C=CHR$) hydrogenation with Wilkinson's catalyst, $(Ph_3P)_3RhCl$.

overall rxn is $H_2C=CHR + H_2 \longrightarrow H_3C-CH_2R$

$(Ph_3P)_3RhCl$ is a square-planar complex, $L = PPh_3$, S = solvent



No Organic Crib

4-29-06

Written by
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Physical Cumulative Exam

April 29, 2006

Solutions

a. Raoult's Law says

$$P_{B(c)}\,(80.1^\circ C) = P^\circ_{B(c)}\,(80.1^\circ C)\; X_{B(c)} \qquad (1)$$

where $P_{B(c)}$ is the vapor pressure of $B(c)$ is the vapor pressure above a $B + C$ solution with mol fractions X_B and X_C and $P^\circ_{B(c)}$ is the vapor pressure above pure liquid $B(c)$ with $X_B = 1$ ($X_C = 1$) at the same temperature.

Since benzene boils at $80.1\,^\circ C$ and since camphor, from info given may be assumed to be nonvolatile at $80.1^\circ C$, it follows from Eq. (1) that

$$P_B\,(80.1^\circ C) = 1\,atm\; X_B \quad \text{and} \quad P_C\,(80.1^\circ C) = 0\,atm \qquad (2)$$

Also $X_B + X_C = 1$ or $X_B = 1 - X_C = 1 - 0.27 = 0.73$. Thus

$$P_B\,(80.1^\circ C) = (1\,atm)(0.73) = 0.73\,atm. \qquad (3)$$

But the vapor pressure $P = P_B + P_C$ or using Eqs. (2) and (3)

$$P\,(80.1^\circ C) \text{ for solution} = 0.73\,atm. \qquad (4)$$

b. For benzene-camphore solution

$C = 2$, B and C

$P = 3$, liq. and vap. and solid

$$\therefore \quad \boxed{F = C - P + 2 = 2 - 3 + 2 = \underline{1}} \qquad (5)$$

c. (i) Recall

$$\mu_{B \text{ or } C,\, \text{vapor or s}} = \left[\frac{\partial G}{\partial n_{B \text{ or } C,\, \text{vapor or s}}}\right]_{T,P} \qquad (6)$$

Also for equilibrium

$$dG_{T,P} = 0 \qquad (7)$$

Combining Eqs. (6) and (7) gives

$$dG_{T,P} = \left[\frac{\partial G}{\partial n_{B_v}}\right]_{T,P} dn_{B_v} + \left[\frac{\partial G}{\partial n_{C_v}}\right]_{T,P} dn_{C_v} + \left[\frac{\partial G}{\partial n_{B_\ell}}\right]_{T,P} dn_{B_\ell} + \left[\frac{\partial G}{\partial n_{C_\ell}}\right]_{T,P} dn_{C_\ell}$$

$$+ \left[\frac{\partial G}{\partial n_{B_s}}\right]_{T,P} dn_{B_s} + \left[\frac{\partial G}{\partial n_{C_s}}\right]_{T,P} dn_{C_s} = 0.$$

$$= \text{Eq. (1.2) using the definitions of } \mu\text{'s in Eq. (6)} \quad (8)$$

Also using Eq. (1.1) the forms of the μ's may be simplified as follows

$$\mu_{B_v} \equiv \left[\frac{\partial G}{\partial n_{B_v}}\right]_{T,P} = \left[\frac{\partial G_v}{\partial n_{B_v}}\right]_{T,P} \quad \text{and} \quad \mu_{C_v} \equiv \left[\frac{\partial G}{\partial n_{C_v}}\right]_{T,P} = \left[\frac{\partial G_v}{\partial n_{C_v}}\right]_{T,P} \quad (9a)$$

$$\mu_{B_\ell} \equiv \left[\frac{\partial G}{\partial n_{B_\ell}}\right]_{T,P} = \left[\frac{\partial G_\ell}{\partial n_{B_\ell}}\right]_{T,P} \quad \text{and} \quad \mu_{C_\ell} \equiv \left[\frac{\partial G}{\partial n_{C_\ell}}\right]_{T,P} = \left[\frac{\partial G_\ell}{\partial n_{C_\ell}}\right]_{T,P} \quad (9b)$$

and

$$\mu_{B_s} \equiv \left[\frac{\partial G}{\partial n_{B_s}}\right]_{T,P} = \left[\frac{\partial G_s}{\partial n_{B_s}}\right]_{T,P} \quad \text{and} \quad \mu_{C_s} \equiv \left[\frac{\partial G}{\partial n_{C_s}}\right]_{T,P} = \left[\frac{\partial G_s}{\partial n_{C_s}}\right]_{T,P} \quad (9c)$$

(ii). Since the total number of mols n_B given by

$$n_B = n_{B_v} + n_{B_\ell} + n_{B_s}$$

is conserved during phase transitions $dn_B = 0$ or

$$dn_B = dn_{B_v} + dn_{B_\ell} + dn_{B_s} = 0. \quad (10a)$$

Similarily

$$dn_C = dn_{C_v} + dn_{C_\ell} + dn_{C_s} = 0. \quad (10b)$$

Eq. (10) are the same as Eq. (1.3) thus proving Eq. (1.3).

(iii) If the conditions of Eq. (1.4) are true then the left hand side of Eq. (1.2) may be written as

$$\mu_B (dn_{B_v} + dn_{B_\ell} + dn_{B_s}) + \mu_C (dn_{C_v} + dn_{C_\ell} + dn_{C_s}) = ? \qquad (11)$$

where $\mu_B \equiv \mu_{B_v} = \mu_{B_\ell} = \mu_{B_s}$ and $\mu_C \equiv \mu_{C_v} + \mu_{C_\ell} + \mu_{C_s}$.

However comparing Eq. (10) and (11) shows $? = 0$, proving that Eq. (11) is equivalent to the equilibrium condition of Eq. (1.2), thus showing that the condition of Eq. (1.4) is sufficient for three-phase equilibrium.

d. (i) The general three phase (v, ℓ, and s) condition for equilibrium for C is from Eq. (1-4)

$$\mu_{C_v} = \mu_{C_\ell} = \mu_{C_s}. \qquad (12)$$

However since C is non-volatile there is no equilibrium between ℓ and v forms of C. Thus Eq. (12) simplifies to the condition

$$\mu_{C_\ell} = \mu_{C_s} \qquad (12')$$

Next note that since G_ℓ is extensive from Eq. (1.)

$$G_\ell = G_\ell (T, P, n_{B_\ell}, n_{C_\ell}) = n\, G_\ell (T, P, X_{B_\ell}, X_{C_\ell}) \qquad (13)$$

where $n = n_{B_\ell} + n_{C_\ell}$ and $X_{B_\ell(C_\ell)} = \dfrac{n_{B_\ell(C_\ell)}}{n}$ = mol fraction.

Thus from the definition of μ_{C_ℓ} in Eq. (4.6),

$$\mu_{C_\ell} = \mu_{C_\ell} (T, P, X_{B_\ell}, X_{C_\ell}) \overset{\text{since } X_{B_\ell} = 1 - X_{C_\ell}}{=} \mu_{C_\ell} (T, P, X_{C_\ell}) \qquad (14a)$$

Similarily

$$\mu_{C_s} = \mu_{C_s} (T, P, X_{B_s}, X_{C_s}) = \mu_{C_s} (T, P, X_{C_s}). \qquad (14b)$$

Thus Eqs. (12') and (14) give the ~~equilib~~ equilibrium condition

$$\mu_{C_\ell}(T, P, X_{C_\ell}) = \mu_{C_s}^*(T, P) \tag{15}$$

where in accord with the assumption that the s phase is pure C we have taken $\mu_{C_s}(T, P, X_{C_s}) = \mu(T, P, X_{C_s} = 1) \equiv \mu_{C_s}^*(T, P)$ the chemical potential of pure solid C.

Solving Eq (1-5) for X_{C_ℓ} allows the mole fraction of C in the ℓ phase to be determined and eventually the solubility with a bit more information

(ii) Since B is not present in the solid, the general condition of equilibrium for B

$$\mu_{B_v} = \mu_{B_\ell} = \mu_{B_s} \tag{16}$$

simplifies to

$$\mu_{B_v}(T, P, X_{B_v}) = \mu_{B_\ell}(T, P, X_{B_\ell}) \tag{17}$$

where we have followed steps similar to those leading from Eqs. (14) and (15). Also since the vapor is pure B we may write $\mu_{B_\ell}(T, P, X_{B_\ell}) = \mu_{B_\ell}(T, P, X_{B_\ell} = 1) = \mu_{B_\ell}^*(T, P)$ = chemical potential of pure vapor B. Thus Eq. (1.6) reduces to the following equation

$$\mu_{B_\ell}(T, P, X_{B_\ell}) = \mu^*(T, P). \tag{18}$$

Assuming P and X_{B_ℓ} are specified the above reduces to an equation for the boiling temperature $T = T(X_{B_\ell}, P)$. The boiling point elevation is $\Delta T = T(X_{B_\ell}, P) - T_B^*(P)$ where $T_B^*(P)$ is the boiling point for pure B at temperature T.

e. Eqs. (1.5) involve the variables T, P, X_{Bv}, X_{Bl}, X_{Bs}, X_{Cv}, X_{Cl}, X_{Cs}. However the conditions provided by Eqs. (1.5) and also the additional conditions $X_C = 1 - X_B$ for s, l, and v render only one of those variables independent. This is in accord with $F = 1$ from part b.