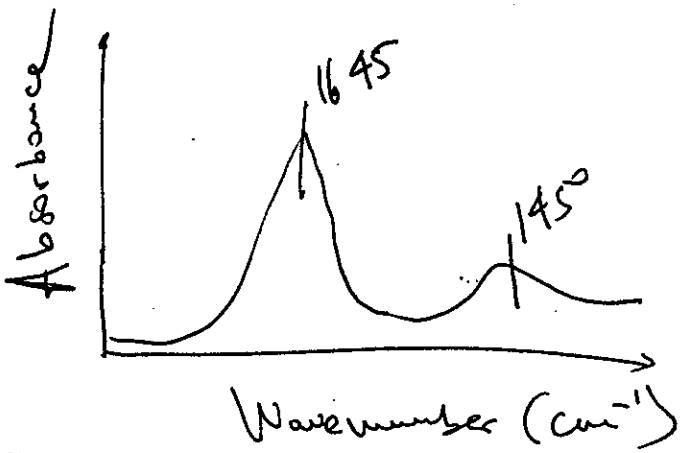
ANALYTICAL CRIB - 4/30/05

Assume that you would like to understand the adsorption behavior of a synthetic peptide to a hydrophilic substrate in-situ using attenuated total reflection infrared spectroscopy (ATR-IR). Suppose that you have successfully modified the ATR crystal to have a hydrophilic surface.

1) Sketch the spectrum that you expect to gather based on the presence of Amide I and Amide II bands.

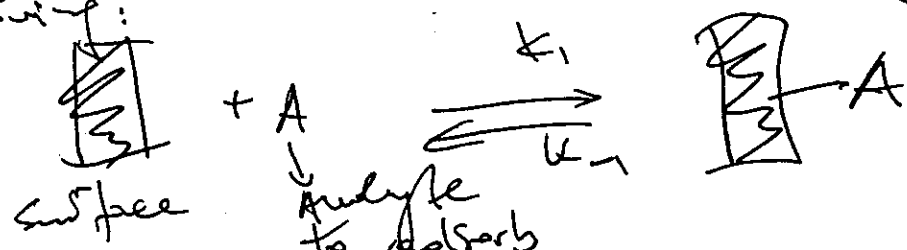


2) Propose an experiment that will help you verify the band assignments.

Assigning bands is difficult → a change of position can be simply due to disorder on the surface.
The best way to verify the assignment is to perform the adsorption under the same conditions w/ an analyte that is labeled.
One can label the Nitrogen (^{14}N naturally more abundant vs ^{15}N). A shift of Amide 20–30 cm⁻¹ is expected.

3) Describe a method to follow the adsorption of the peptide to the crystal surface if you assume Langmuirian behavior. Describe how you will determine coverage at a given concentration of ~~A~~ peptide to which the surface was exposed. (Note you will not receive any points for simply stating the assumptions of the Langmuir adsorption isotherm).

Briefly the isotherm is the following:



$$k_1 [1-\theta][A] = k_{-1}\theta$$

$$\theta = \frac{K[A]}{K[A]+1} \quad \text{or} \quad \frac{1}{\theta} = \frac{1}{K[A]} + 1$$

over

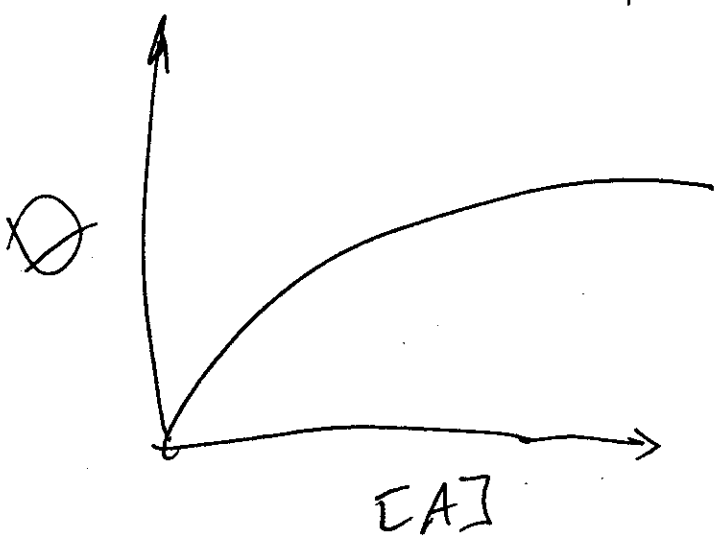
θ is the fractional surface coverage.

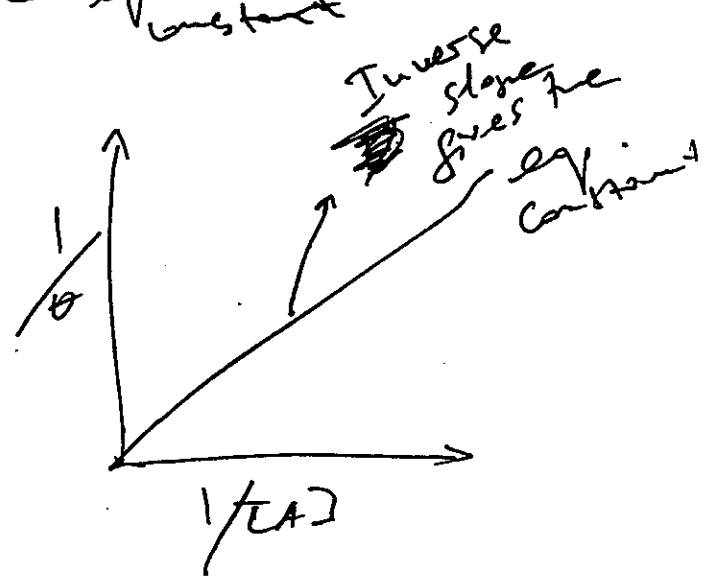
at $[A] = 0$ $\theta = 0$

at $[A]$ = saturation $\theta = 1$

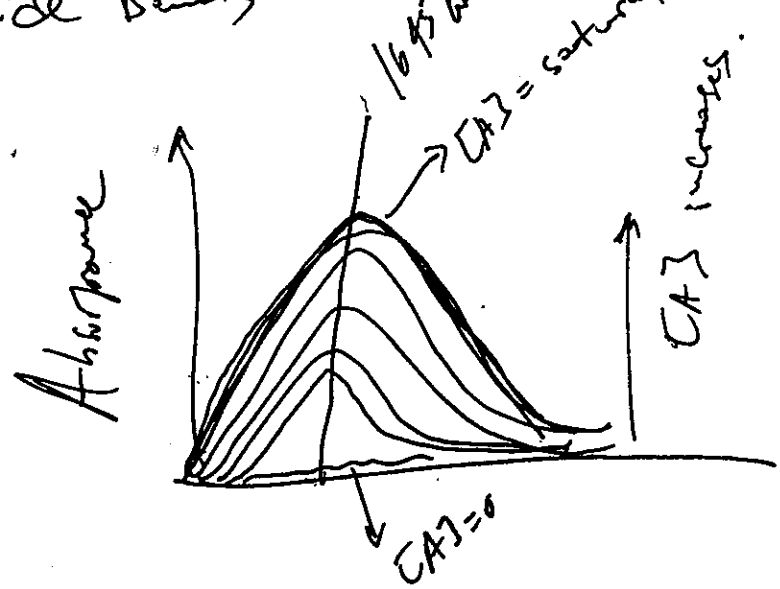
Therefore based on the assumptions of the isotherm one gets a typical isotherm line like:

K is the equilibrium constant





In a typical experiment one can monitor the Abs at one of the Amide bands



③

The isotherm assumes that:

- Adsorption does not go beyond a monolayer coverage
- All sites on the surface are equal -
- A molecule's ability to adsorb at a given site is independent of what happens at neighboring sites:

Therefore

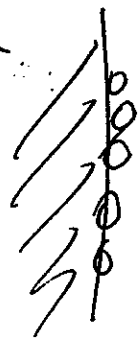
1) at $[A]=0$

$\theta = 0$

2) $[A]_1 > 0.1\ \mu M$

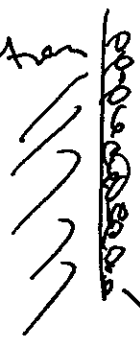
θ = some fraction

3) $[A]_1 < [A]_2 > 0\ \mu M$



θ = some bigger fraction.

4) $[A]_3 > 0$ = saturation



$\theta = 1$

All sites are occupied.

→

(4)

Sample data set to collect from the ATR-IR experiment

Abs of 1645	Conc		θ
baseline value ----	0		0
a			
b			
c			
d			
k	X	μM	1
k	X<Y	μM	1
k	Y<Z	μM	1

The concentration increases

as the concentration increases

when saturation is reached by this point

Fraction coverages (θ) can be calculated from

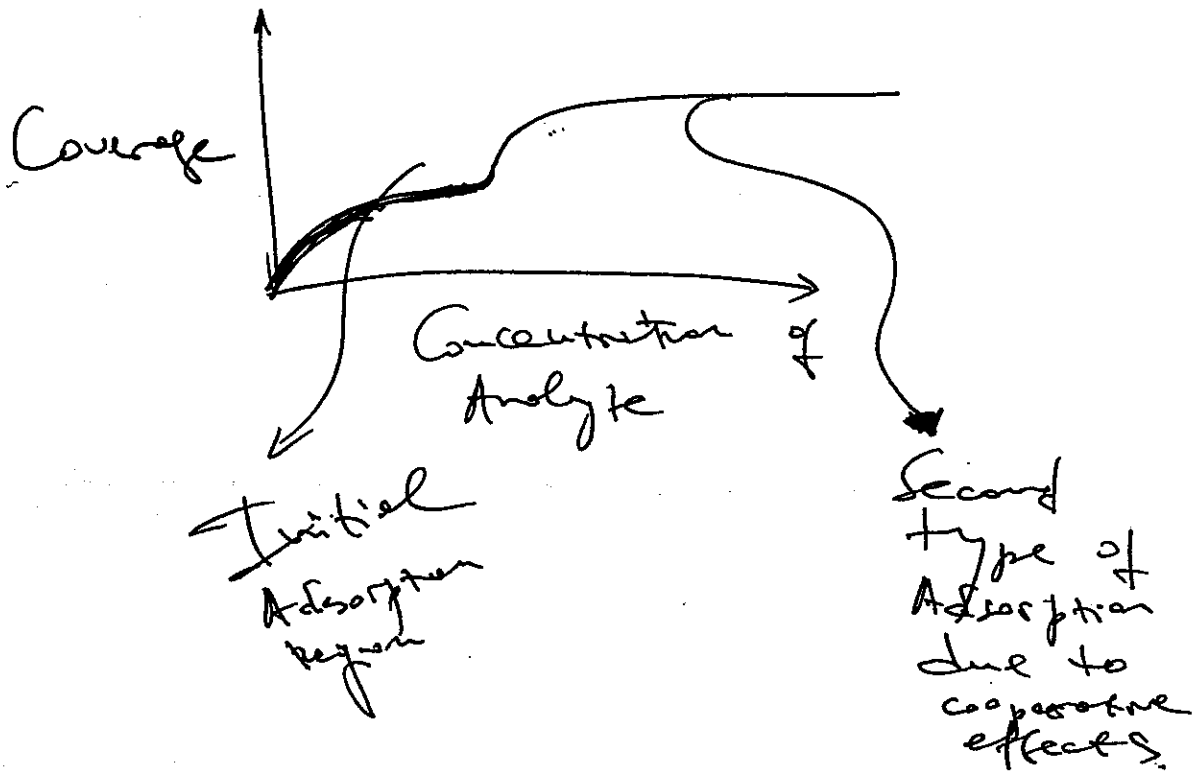
$$\theta = \frac{\left| Abs_{given\ conc.} - Abs_{ref} \right|}{\left| Abs_{sat} - Abs_{ref} \right|}$$

Using the table one can construct θ vs conc. 1/θ vs 1/[E] and calculate K.

(5)

4) Does the Langmuir adsorption isotherm work if a cooperative effect is taking place?

In the event that cooperative effects are taking place the Isotherm will not be simple. Likely one will observe a two step process



* One can still fit each portion of the isotherm to the model in a two step process.

APRIL 30, 2005

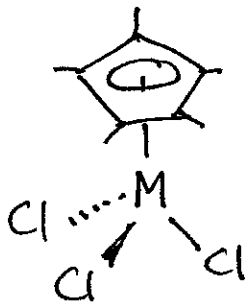
Biochemistry Cumulative Examination Crib

See Professor Kavita Shah

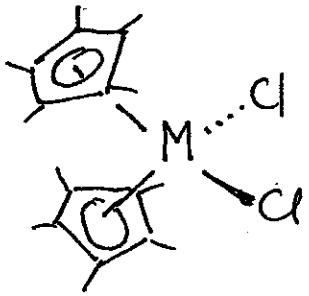
INORGANIC CHEME EXAM – CRIB

April 30, 2005

1)

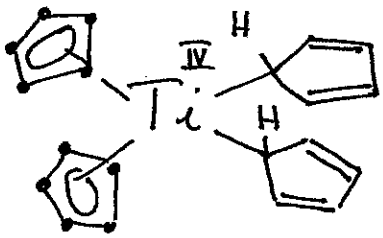


electron count 12



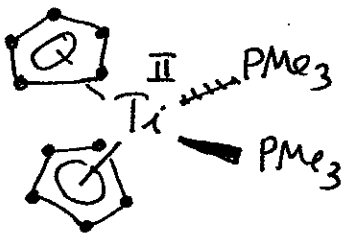
electron count 16

(i)



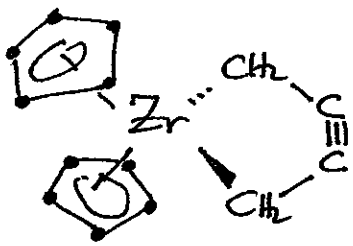
electron count 16

(ii)



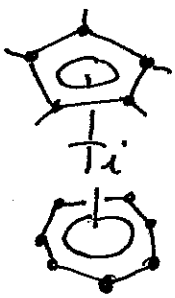
electron count 18

(iii)



electron count 16

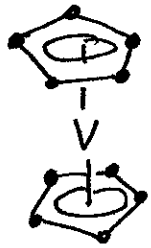
(iv)



electron count 16

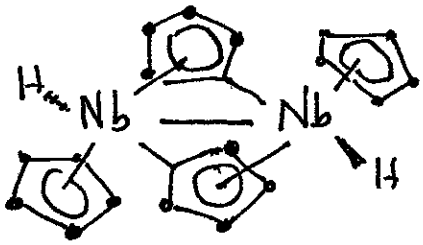
2).

M=V

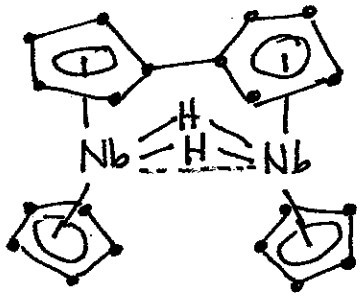


15-e molecule

M = Nb

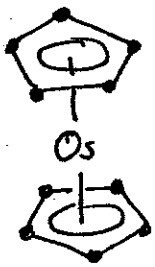


and



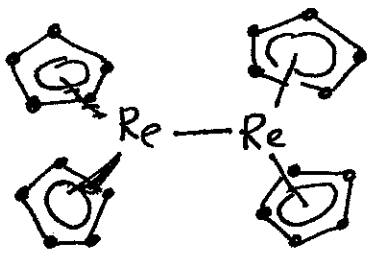
i.e. two structural isomers both of which have non-sandwich structures

M= Os



18-e molecule

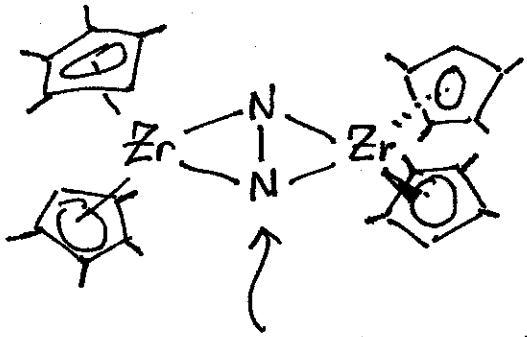
M= Re



Cp_2Re would have a 17-e metal count. The Re–Re bonded structure has an 18-e count

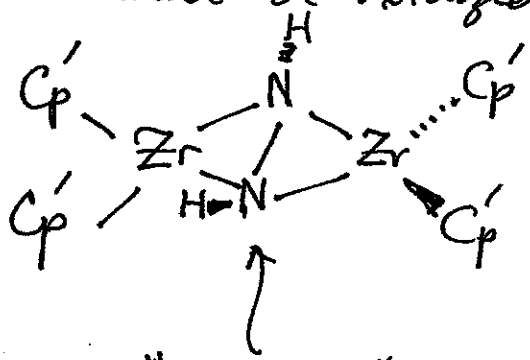
While most bis-Cp complexes of the 1st transition series have the ferrocene type of sandwich structure ($(C_5H_5)_2Ti$ and $(C_5H_5)_2Mn$ are exceptions), many of the 2nd and 3rd transition series do not. The <u>early transition elements</u> Zr, Hf, Nb, Ta, Mo and W have more complicated structures (like Nb), which most likely reflects the comparative ease of oxidizing the M(II) oxidation state, as would be present in a $(\eta^5\text{-}C_5H_5)_2M$ structure. In the case of niobocene, there are two structural forms, both of which contain contain diniobium units and Nb in a higher oxidation state. Osmocene, like its ferrocene congener, has a stable 18-electron count and, therefore, has a sandwich structure. If rhenocene were $(\eta^5\text{-}C_5H_5)_2Re$, it would have a 17-electron count; it dimerizes by forming a Re–Re bond to give a more stable 18-electron molecule.

3). **A** is



planar Zr–N(–N)–Zr unit that contains a long N–N distance (1.377(3) Å) consistent with reduced "N_2" – therefore, the Zr must be oxidized (Zr(IV)?)

B is



Cp' = C_5Me_4H

"diazenido"-like ligand

<u>First example</u> of the hydrogenation of N_2 in a well-defined dinitrogen complex.

<u>Note</u>: Further hydrogenation at a higher T gives $(\eta^5\text{-}C_5Me_4H)_2ZrH_2$ + a low yield of NH_3.

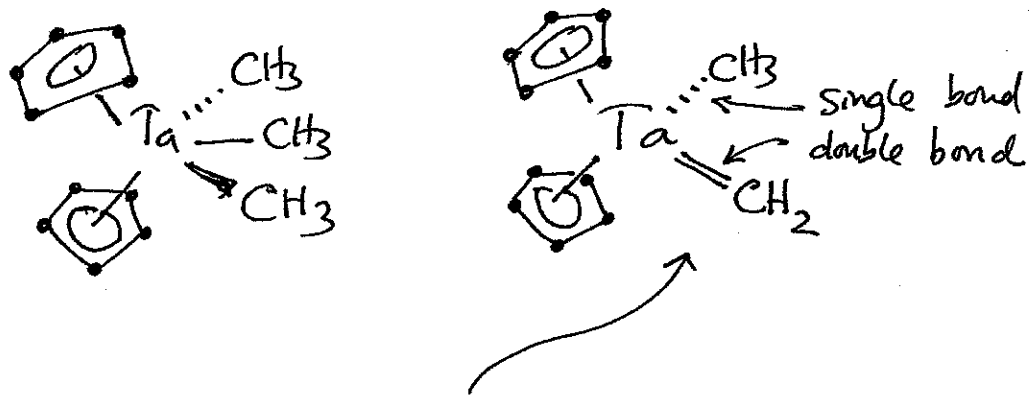
4) (i) $2\,TaCl_5 + 3\,Me_2Zn \longrightarrow 2(CH_3)_3TaCl_2 + 3ZnCl_2$

(ii) $(CH_3)_3TaCl_2 + 2(C_5H_5)Tl \longrightarrow (\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3 + 2TlCl\downarrow$

(iii) $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_3 + \underset{\text{(electrophile)}}{Ph_3C^+BF_4^-} \longrightarrow [(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2]^+BF_4^- + Ph_3CCH_3$

(iv) $[(\eta^5\text{-}C_5H_5)_2Ta(CH_3)_2]^+BF_4^- + \underset{\text{(strong base)}}{Li[N(SiMe_3)_2]}^{*} \longrightarrow (\eta^5\text{-}C_5H_5)_2Ta(CH_3)(CH_2) + (Me_3Si)_2NH + Li^+BF_4^-$

* Other strong bases such as $Me_3P{=}CH_2$ or NaOMe can be used

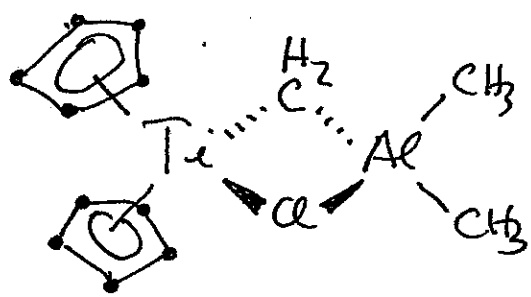


<u>Special significance</u>: example of an alkylidene (carbene) complex formed by an <u>intermolecular</u> α-H abstraction reaction (of the cationic dimethyl intermediate).

5). Tebbe's reagent is $Cp_2Ti(CH_2)(Cl)Al(CH_3)_2$

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + 2\,Al(CH_3)_3 \longrightarrow$$
$$(\eta^5\text{-}C_5H_5)_2Ti(CH_2)(Cl)Al(CH_3)_2 + CH_4 + AlCl(CH_3)_2$$

or $$(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2 + AlCl(CH_3)_2 \longrightarrow$$
$$(\eta^5\text{-}C_5H_5)_2Ti(CH_2)(Cl)Al(CH_3)_2 + CH_4$$

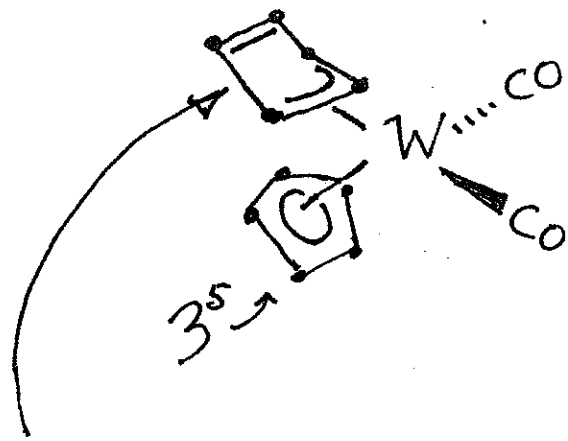


Tebbe's reagent is used for methylene transfer as in the homologation of olefins and the conversion of ketones to terminal olefins.

b) A good example of a complex that contains a η^3-C_5H_5 ligand is

$$(C_5H_5)_2W(CO)_2$$

If both C_5H_5 ligands were η^5-bound this compound would have a 20-electron count for the metal. In order not to exceed the stable 18-electron count one of the Cp rings binds as an η^3-ligand



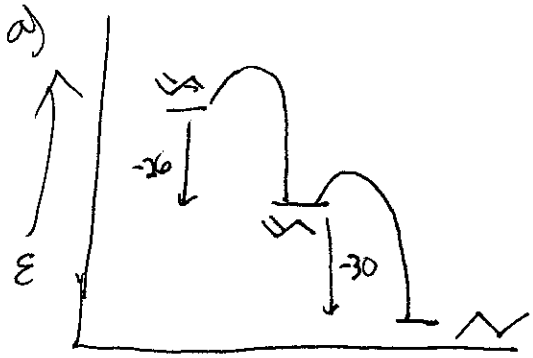
Electron count	
W	6
2×CO	4
η^5-Cp	5
η^3-Cp	3
	18-e

η^3- non-planar (folded) ring which behaves like an allyl-ene

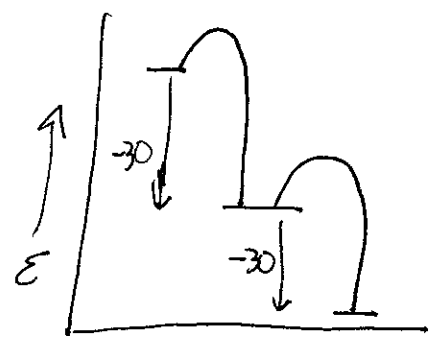
25pts 1) a) 1 CH_3 3 iC_3H_7
2 C_2H_5 4 tC_4H_9

b) The best approach for assessing radical stabilities is reactivity. Bond dissociation energies are not appropriate because they reflect the properties of reactants and products

20pts 2) a)



b)



The first reaction energy is larger because the reactant is higher in energy because it is not stabilized by conjugation

20pts 3)

$-\alpha - 1.618\beta$
$-\alpha - .618\beta$
$\uparrow\downarrow\ \alpha + .618\beta$
$\uparrow\downarrow\ \alpha + 1.618\beta$

$E_{TOT} = 2(\alpha + 1.618\beta) + 2(\alpha + .618\beta)$
$= 4\alpha + 4.472\beta$

Non-resonant model: 2 × Energy of ethylene $= 2(2\alpha + 2\beta)$
$E_{Res} = 4\alpha + 4.472\beta - (4\alpha + 4\beta) = .472\beta$

Assuming $\beta \approx 18$ kcal/mol gives $E_{Res} \approx 8$ kcal/mol
Hawk value: 8.2 kcal/mol

15 pts 4) a) 9.3 Kcal/mol

b) The Kistiakovsky approach fails because it does 7
not distinguish between stabilization due to conjugation 14
or for other reasons, including hyperconjugation 20

Note: It is <u>Not</u> correct to say that the Kistiakovsky approach does not include hyperconjugation – the problem is that it <u>does</u> include hyperconjugation, and the hyperconjugation has to be taken out for proper analysis – that is what Houk's paper did

20 pts 5) Kistiakovsky compared the heat of hydrogenation of benzene with $3 \times \Delta H_{hyd}$ of cyclohexene

$E_{RES} = 36$ kcal/mol

Using E_{RES} ( ) $= 2\beta$, that gives $\beta = 18$ kcal/mol

#1 ⓐ $dE = TdS - pdV + \mu dN + \gamma da$

$$dG = dE - TdS - SdT + pdV + Vdp$$

$$dG = -S\cancel{dT} + V\cancel{dp} + \mu\cancel{dN} + \gamma da$$

ϕ constant T & P; ϕ; closed system

$$dG = \gamma da$$

$$\boxed{\gamma = \left(\frac{dG}{da}\right)_{T,P,N}}$$

ⓑ $\left(\frac{\partial S}{\partial a}\right)_{P,T}$ $\quad dE = TdS - pdV + \mu dN + \gamma da$

if $df = adx + bdy$ then $\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y$

view S as a fn of a, P & T

need Gibbs: $dG = -SdT + Vdp + \cancel{\mu dN} + \gamma da$ closed system

$$\boxed{\left(\frac{\partial S}{\partial a}\right)_{P,T} = -\left(\frac{\partial \gamma}{\partial T}\right)_{a,P}}$$

$$\gamma(T) = b - cT$$

$$\boxed{\frac{d\gamma}{dT} = +c = +0.1670 \text{ erg/cm}^2\text{ deg}}$$

ⓒ $\frac{\Delta S}{\Delta a} = -c$ $\quad \Delta S = +c\Delta a = (+0.1670 \text{ erg/cm}^2\text{ deg})(4\text{ Å}^2)$

$$\boxed{= +6.68\times10^{-17} \text{ erg/deg}}$$

#2. The units of entropy are J/K

① $S = \left(\frac{k_B^2}{V_0 \theta}\right)^{1/3} (EVN)^{1/3}$ $\left(\frac{J^2/K^2}{m^3 K}\right)^{1/3} \left(J m^3\right)^{1/3} \rightarrow \frac{J}{K}$

② $S = \left(\frac{k_B V_0^2}{\theta^2}\right)^{1/3} \left(\frac{EN}{V}\right)^{2/3}$ $\left(\frac{(J/K) m^6}{K^2}\right)^{1/3} \left(\frac{J}{m^3}\right)^{2/3} \rightarrow \frac{J}{K}$

③ $S = \left(\frac{k_B V_0^2}{\theta^2}\right)^{1/3} \left(\frac{EN}{V}\right)$ $\left(\frac{(J/K) m^6}{K^2}\right)^{1/3} \left(\frac{J}{m^3}\right) \rightarrow \frac{J^{4/3}}{K \cdot m}$

wrong units

④ $S = \left(\frac{k_B}{\theta}\right)^{1/2} \left(NE - \frac{k_B \theta V^2}{V_0^2}\right)^{1/2}$ $\left(\frac{J/K}{K}\right)^{1/2} \left(J - \frac{(J/K) K m^6}{m^6}\right)^{1/2} \rightarrow \frac{J}{K}$

If $\frac{k_B \theta V^2}{V_0^2} > NE$ i.e. as $T \uparrow$ then entropy will be complex.

) $S = k_B N \ln\left(\frac{EV}{N^2 k_B \theta V_0}\right)$ $\left(\frac{J m^3}{J/K\ K\ m^3}\right)$ unitless ✓

) $S = k_B N \exp\left(\frac{-EV}{N^2 k_B V_0}\right)$ $\left(\frac{J m^3}{J/K\ m^3}\right)$ not unitless

The stuff in the exponent has to be unitless

) $S = k_B N \exp\left(\frac{-EV^2}{N^2 k_B \theta V_0}\right)$ $\left(\frac{J m^6}{J/K\ K\ m^3}\right)$

The stuff in the exponent has to be unitless.

2 continued...

Could also eliminate #6 & #7 b/c

$$\left.\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$$ which must be $\geq \phi$

when you take $\left.\frac{\partial S}{\partial E}\right)_V$ a negative sign appears

$$dE = TdS + pdV - \mu dN$$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$\left.\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} > \phi$$

This eliminates # 2 & # 3

$\Rightarrow$ 2, 3, 6 & 7 are definitely incorrect

and # 5 is also possibly incorrect

#3

$$dE = TdS - pdV + \mu dN$$

$$TdS = dE + pdV - \mu dN$$

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \cancel{\frac{\mu}{T}dN} \rightarrow \phi \quad \text{fixed } N$$

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V}$$

#4 (a) $\left(\frac{\partial \beta p}{\partial \rho}\right)_\beta = \left(\frac{\partial^2 \beta p}{\partial \rho^2}\right)_\beta = \phi$ $\qquad \beta p = \frac{\rho}{(1-b\rho)} - \beta a \rho^2$

$$\beta p = \rho(1-b\rho)^{-1} - \beta a \rho^2$$

$$\left(\frac{\partial \beta p}{\partial \rho}\right)_\beta = (1-b\rho)^{-1} - \rho(1-b\rho)^{-2}(-b) - 2\beta a \rho$$

$$= \frac{(1-b\rho) + b\rho}{(1-b\rho)^2} - 2\beta a \rho$$

$$= \frac{1}{(1-b\rho)^2} - 2\beta a \rho = (1-b\rho)^{-2} - 2\beta a \rho = 0$$

$$\left(\frac{\partial^2 \beta p}{\partial \rho}\right)_\beta = -2(1-b\rho)^{-3}(-b) - 2\beta a = \frac{2b}{(1-b\rho)^3} - 2\beta a = 0$$

let's get rid of β $\qquad 2\beta a = \frac{2b}{(1-b\rho)^3}$

so $\frac{1}{(1-b\rho)^2} - \frac{2b\rho}{(1-b\rho)^3} = 0$

$$\frac{1}{\ldots} = \frac{2b\rho}{\ldots^3} \qquad 1 = \frac{2b\rho}{(1-b\rho)}$$

$$1 - b\rho = 2b\rho$$

$$1 = 3b\rho$$

$$\boxed{\rho_c = \frac{1}{3b}}$$

now $$2\beta a = \frac{2b}{(1-b\rho)^3}$$

$$\beta_c = \frac{\cancel{2}b}{\cancel{2}a\left(1-\cancel{b}\left(\frac{1}{3\cancel{b}}\right)\right)^3}$$

$$= \frac{b}{a\left(\frac{2}{3}\right)^3} = \boxed{\frac{27b}{8a}}$$