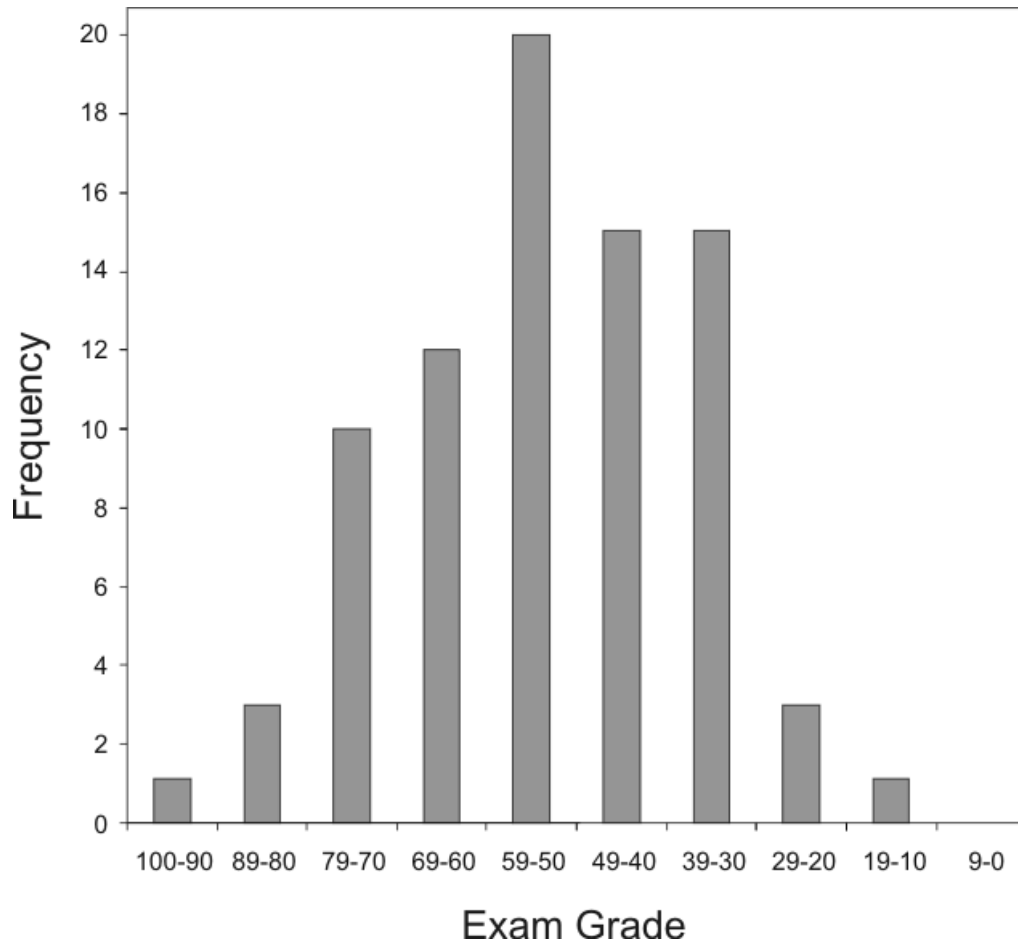


**Exam 2
Answer Key**

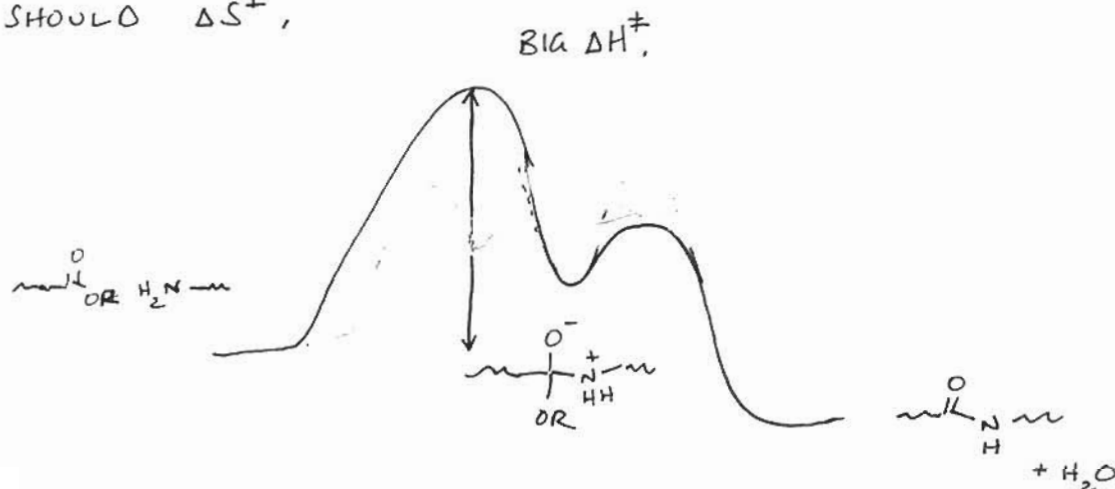
Exam 1 Mean: 49
Exam 1 Median: 48
Exam 1 St. Dev.: 16



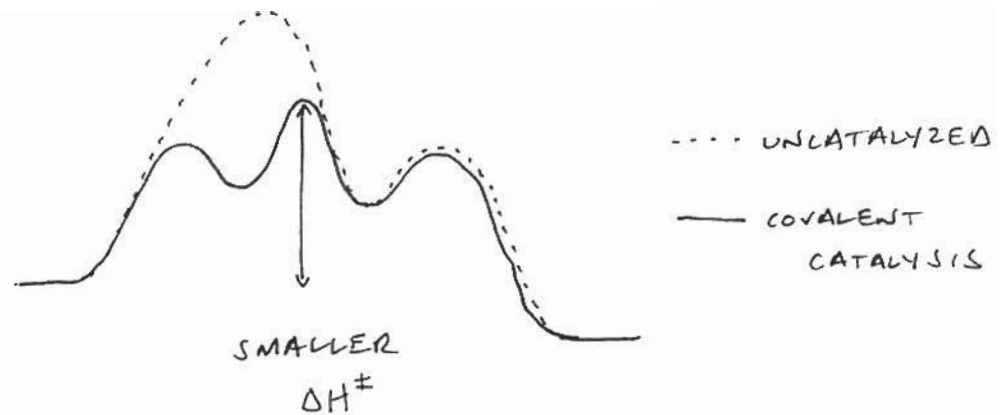
EXAM 2 ~~2004~~ 2004

ANSWER KEY

1. a) FOR EACH MECHANISM, THE ΔH^\ddagger AND ΔS^\ddagger SHOULD REFLECT CHANGES IN THE RATE DETERMINING STEP. FOR THE UNCATALYZED REACTION, GOING FROM STARTING MATERIAL TO THE TETRAHEDRAL INTERMEDIATE IS ENDOTHERMIC, AND ΔH^\ddagger SHOULD BE LARGE (AND POSITIVE, BY DEFINITION). BECAUSE THIS STEP INVOLVES CREATING ONE INTERMEDIATE MOLECULE FROM TWO STARTING MOLECULES, OVERALL ΔS° SHOULD BE NEGATIVE FOR THIS STEP, AND LIKEWISE SHOULD ΔS^\ddagger ,



IF THE RIBOSOME WERE TO CATALYZE THIS REACTION BY MECHANISM A, IT WOULD BE BY CREATING ANOTHER INTERMEDIATE IN THE FIRST STEP ABOVE:



IN THIS CASE, $\Delta H^\ddagger(\text{mech. A}) < \Delta H^\ddagger(\text{uncat.})$. BUT THE RATE-DETERMINING STEP STILL BRINGS TWO REACTANTS TOGETHER TO ONE INTERMEDIATE, SO I WOULD GUESS ΔS^\ddagger WOULD BE ABOUT THE SAME.

IN MECHANISM B, THE ENZYME DOESN'T AID THE ENTHALPY OF MAKING OR BREAKING BONDS AT ALL; THE SAME NUCLEOPHILIC AMINE ATTACKS THE SAME ELECTROPHILE ESTER, AND SO I WOULDN'T EXPECT MECHANISM B TO CHANGE ΔH^\ddagger . BUT THE RIBOSOME IN MECHANISM B DOES MAKE IT SUCH THAT ONLY ONE MOLECULAR SPECIES STARTING MATERIAL (THE RIBOSOME-POLYPEPTIDE-ESTER COMPLEX) TURNS INTO ONE MOLECULAR PRODUCT. I'D EXPECT ΔS^\ddagger TO BE ABOUT ZERO FOR THIS PROCESS - CERTAINLY LESS THAN IN MECHANISM A OR THE UNCATALYZED CASE.

<, >, or =

| | | |
|---|-----------|---|
| $\Delta H^\ddagger(\text{uncatalyzed})$ | $>$ | $\Delta H^\ddagger(\text{mechanism A})$ |
| $\Delta H^\ddagger(\text{uncatalyzed})$ | \approx | $\Delta H^\ddagger(\text{mechanism B})$ |
| $\Delta H^\ddagger(\text{mechanism A})$ | $<$ | $\Delta H^\ddagger(\text{mechanism B})$ |
| $\Delta S^\ddagger(\text{uncatalyzed})$ | \approx | $\Delta S^\ddagger(\text{mechanism A})$ |
| $\Delta S^\ddagger(\text{uncatalyzed})$ | $<$ | $\Delta S^\ddagger(\text{mechanism B})$ |
| $\Delta S^\ddagger(\text{mechanism A})$ | $<$ | $\Delta S^\ddagger(\text{mechanism B})$ |

3 POINTS EACH,
ALL OR NOTHING.

b) ~~PLEASE READ THE QUESTIONS CAREFULLY~~

EITHER GRAPH ON PAGE 2 COULD BE USED TO ANSWER THIS QUESTION. THE GRAPH ON THE LEFT IS AN ARRHENIUS PLOT, AND WOULD REQUIRE YOU TO CALCULATE E_a & A AND THEN CONVERT TO ΔH^\ddagger AND ΔS^\ddagger . THE GRAPH ON THE RIGHT IS AN EYRING PLOT, AND ALLOWS YOU TO DETERMINE ΔH^\ddagger AND ΔS^\ddagger DIRECTLY.

BY ~~THE~~ ARRHENIUS METHOD:

$$k_{rxn} = A e^{-E_a/RT}$$
$$\ln k_{rxn} = \left(\frac{-E_a}{R}\right) \left(\frac{1}{T}\right) + \ln A \quad (\text{form } y = mx + b)$$

RIBOSOME -
~~THE~~ CATALYZED:

$$\text{SLOPE} = -8.31 \times 10^3 \text{ K} = \frac{-E_a}{R}$$

$$E_a = 16.54 \text{ kcal/mol} = 69.19 \text{ kJ/mol}$$

$$\text{INTERCEPT} = 34.2 = \ln A$$

$$A = 7.13 \times 10^{14}$$

$$\Delta H^\ddagger = E_a - RT; \quad \text{AT } 298 \text{ K,}$$

$$\Delta H^\ddagger = 15.9 \text{ kcal/mol} = 66.9 \text{ kJ/mol}$$

$$\Delta S^\ddagger = R \ln \left(\frac{Ah}{eKT} \right); \quad \text{AT } 298 \text{ K,}$$

$$\Delta S^\ddagger = 7.67 \text{ cal/mol}\cdot\text{K} = 32.1 \text{ J/mol}\cdot\text{K}$$

UNCATALYZED:

$$\text{SLOPE} = -6.65 \times 10^3 \text{ K} = -E_a/R$$

$$E_a = 13.2 \text{ kcal/mol} = 55.4 \text{ kJ/mol}$$

$$\text{INTERCEPT} = 12.4 = \ln A$$

$$A = 2.43 \times 10^5$$

$$\Delta H^\ddagger = E_a - RT; \quad \text{AT } 298 \text{ K,}$$

$$\Delta H^\ddagger = 12.6 \text{ kcal/mol} = 52.7 \text{ kJ/mol}$$

$$\Delta S^\ddagger = R \ln \left(\frac{Ah}{eKT} \right); \quad \text{AT } 298 \text{ K,}$$

$$\Delta S^\ddagger = -35.7 \text{ cal/mol}\cdot\text{K} = -149 \text{ J/mol}\cdot\text{K}$$

(THIS WAS THE HARD WAY.)

BY EYRING METHOD:

$$\ln \left(\frac{k_{\text{rxn}}}{T} \right) = \left[\underbrace{\ln \left(\frac{k}{h} \right)}_{\text{intercept}} + \frac{\Delta S^\ddagger}{R} \right] + \underbrace{\left(\frac{-\Delta H^\ddagger}{R} \right)}_{\text{slope}} \left(\frac{1}{T} \right)$$

(form $y = b + mx$)

RIBOSOME-CATALYZED:

$$\text{SLOPE} = \frac{-\Delta H^\ddagger}{R} = -8.04 \times 10^3 \text{ K}$$

$$\Delta H^\ddagger = 16.0 \text{ kcal/mol} = 66.9 \text{ kJ/mol}$$

$$\text{INTERCEPT} = \ln\left(\frac{k}{h}\right) + \frac{\Delta S^\ddagger}{R} = 27.4$$

$$\Delta S^\ddagger = 7.2 \text{ cal/mol}\cdot\text{K} = 30.3 \text{ J/mol}\cdot\text{K}$$

UNCATALYZED:

$$\text{SLOPE} = \frac{-\Delta H^\ddagger}{R} = -6.38 \times 10^3 \text{ K}$$

$$\Delta H^\ddagger = 12.7 \text{ kcal/mol} = 53.1 \text{ kJ/mol}$$

$$\text{INTERCEPT} = \ln\left(\frac{k}{h}\right) + \frac{\Delta S^\ddagger}{R} = 5.69$$

$$\Delta S^\ddagger = -35.9 \text{ cal/mol}\cdot\text{K} = -150 \text{ J/mol}\cdot\text{K}$$

SO, TO SUM UP:

ΔH^\ddagger (uncatalyzed)

13 kcal/mol OR

53 kJ/mol

ΔH^\ddagger (ribosome-catalyzed)

16 kcal/mol OR

67 kJ/mol

ΔS^\ddagger (uncatalyzed)

-36 cal/mol·K OR

-150 J/mol·K

ΔS^\ddagger (ribosome-catalyzed)

7.5 cal/mol·K OR

31 J/mol·K

3 POINTS EACH BOX.

ANSWERS SHOULD BE WITHIN ~~20%~~ 20%.

ONLY 1 POINT OFF PER BOX IF

- UNITS ARE INCORRECT OR MISSING, BUT NUMBER CORRECT;
- POSITIVE/NEGATIVE SIGN INCORRECT, BUT NUMBER CORRECT.

c) MECHANISM B IS CORRECT; AS PREDICTED IN PART (a), $\Delta S^\ddagger(\text{ribosome}) \gg \Delta S^\ddagger(\text{uncatalyzed})$, AND $\Delta H^\ddagger(\text{ribosome}) \approx \Delta H^\ddagger(\text{uncatalyzed})$. IN TERMS OF MECHANISM, THIS IS BECAUSE MOLECULARITY OF REACTION IS DECREASED BY RIBOSOME ($1 \rightarrow 1$), BUT AMIDE FORMATION IS NOT APPRECIABLY CHANGED.

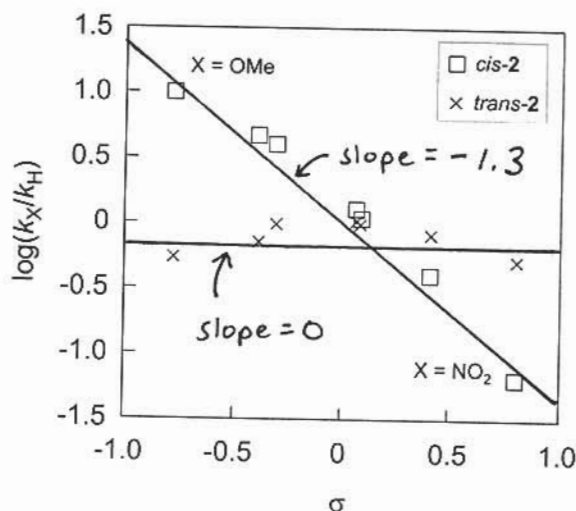
5 POINTS FOR MECHANISM B.

10 POINTS FOR ESSAY.

- 5 POINTS FOR ~~ENTERING~~ DISCUSSING ENTROPY[‡] FOR MECHANISM B. MUST TALK ABOUT MOLECULES (NOT JUST NUMBERS).
- 5 POINTS FOR DISCUSSING (LACK OF CHANGE IN) ΔH^\ddagger FOR MECHANISM B, SAME CRITERION.

2. TOUGH PROBLEM, WITH A TWIST OR TWO.

a) DRAWING ONE LINE THROUGH SQUARES AND THE OTHER THROUGH X'S,



$$\log \frac{k_x}{k_H} = \sigma \rho$$

↑
slope

so,

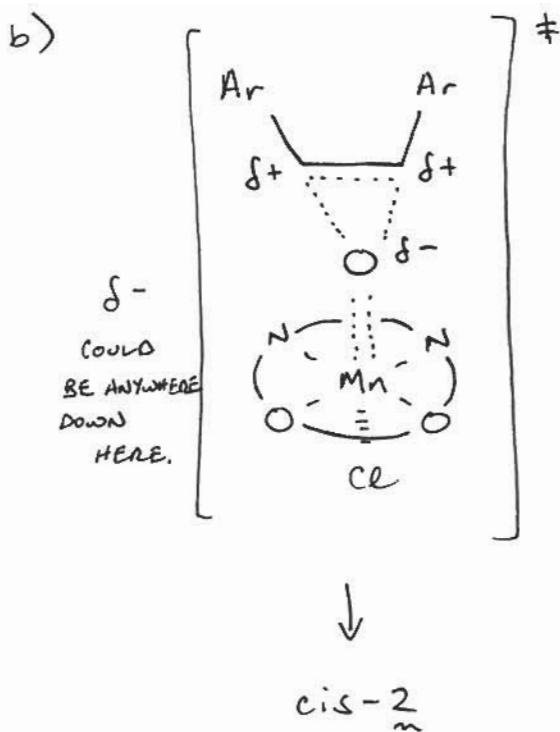
$$\rho_{cis} = -1.3$$

$$\rho_{trans} = 0$$

5 POINTS EACH; ± 0.2 IS ACCEPTABLE.
2 POINTS IF $\rho_{cis} = +1.3$.

WHAT DOES THIS ILLUSTRATE?

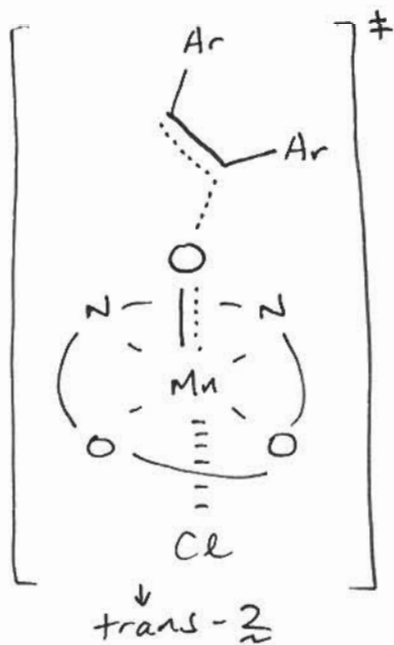
- FOR THE CONCERTED FORMATION OF cis-2,
ELECTRON-DONATING GROUPS ACCELERATE AND
ELECTRON-WITHDRAWING GROUPS SLOW REACTION,
~~***~~ SOMEWHERE IN TRANSITION-STATE, THERE
MUST BE POSITIVE CHARGE, TO STABILIZE/DESTABILIZE
- FOR STEPWISE FORMATION OF trans-2,
ELECTRON-DONATING/-WITHDRAWING GROUPS
HAVE NO PARTICULAR EFFECT.



THIS WAS ONE OF THE TWISTS, ODDLY, EVEN THOUGH THE CONCERTED MECHANISM STARTS NEUTRAL, ENDS NEUTRAL, THE ARYL GROUPS MUST INTERACT w/ A (PARTIAL) POSITIVE CHARGE IN THE TRANSITION STATE. T.S. IS SORT OF DIFFERENT FROM EITHER STARTING MATERIALS OR PRODUCTS.

7 POINTS FOR THIS ONE.

- 4 POINTS FOR NET POSITIVE PARTIAL CHARGE ON TWO BZ CARBONS;
- 3 POINTS FOR ~~THREE~~ DOTTED BONDS. 1 OF THESE POINTS IS FOR SYMMETRIC T.S. STRUCTURE



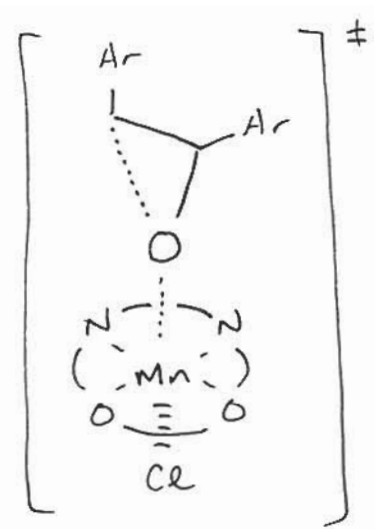
SINCE $\rho_{trans} \approx 0$, "?" MUST BE A RADICAL. SO NO TOTAL PARTIAL CHARGE IS FELT AT EITHER CARBON.

8 POINTS:

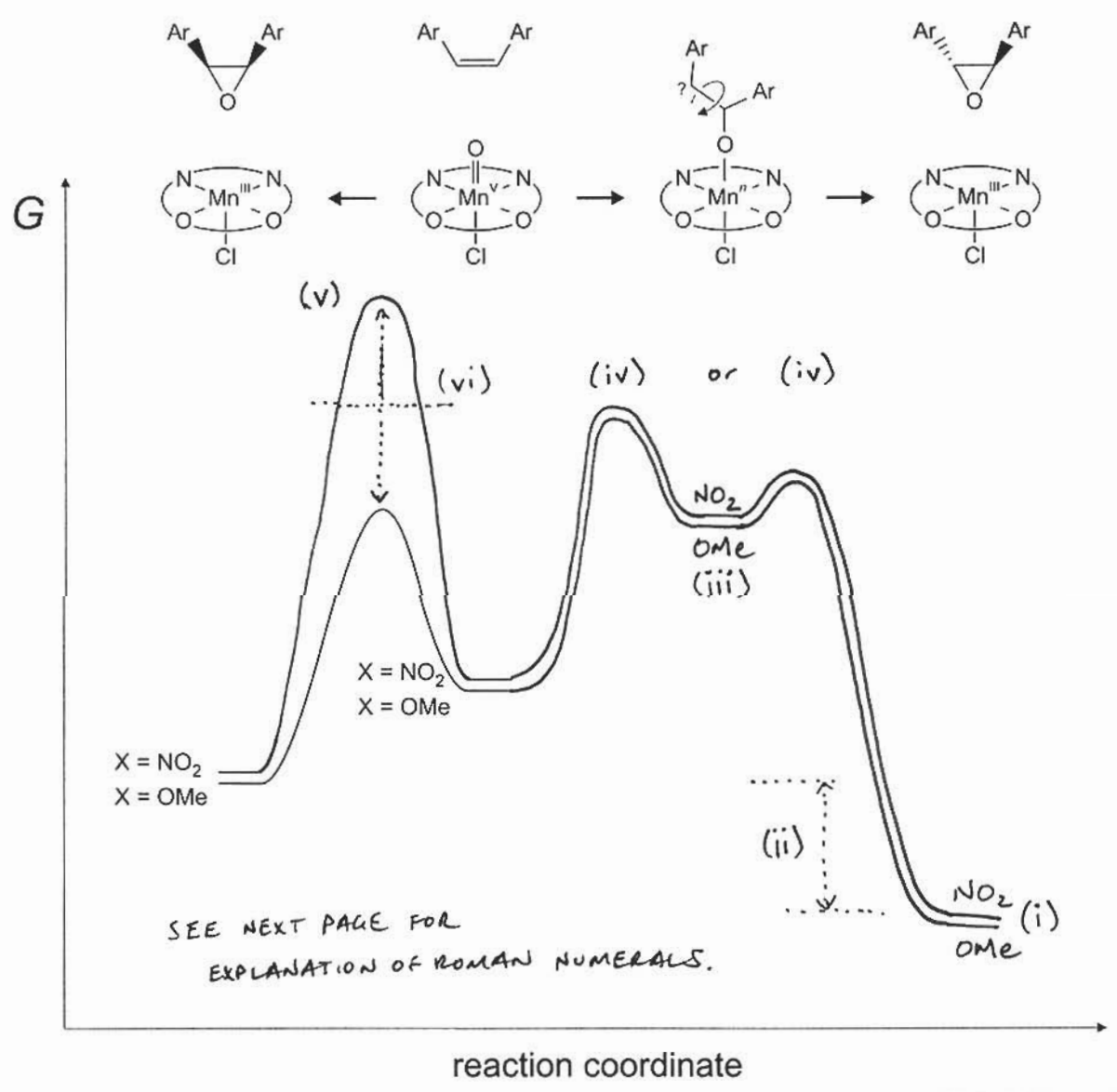
- 4 FOR NO NET CHARGE ON STILBENE CARBONS. CHARGE ELSEWHERE IS FINE.
- 3 FOR CONNECTIVITY / BONDS. MUST BE ASYMMETRIC.

TECHNICALLY, WE DON'T KNOW WHETHER RATE-DETERMINING TRANSITION-STATE FOR TRANS IS FIRST STEP OR SECOND. SO, ALSO POSSIBLE IS: \longrightarrow

SAME GRADING RULES!



c)



KEY FEATURES OF PLOT (w/ POINTS):

- (i) ENERGIES OF $\text{trans-2}(\text{NO}_2)$ AND $\text{trans-2}(\text{OMe})$ ARE THE SAME. (2 POINTS)
- (ii) ENERGIES OF BOTH trans-2 's ARE LOWER THAN cis-2 's. (4 POINTS; 2 FOR EACH cis/trans PAIR).
- (iii) ENERGIES OF $\text{trans-radical-intermediates}$ FOR $X = \text{OMe}$ & $X = \text{NO}_2$ ARE THE SAME, BECAUSE NO CHARGE IS PRESENT. (2 POINTS)
- (iv) HIGHEST TRANSITION STATES ON THE WAY TO $\text{trans-2}(\text{OMe})$ AND $\text{trans-2}(\text{NO}_2)$ ARE AT THE SAME ENERGY. (4 POINTS)
- (v) TRANSITION STATE $\rightarrow \text{cis-2}(\text{NO}_2)$ IS MUCH HIGHER THAN TRANSITION STATE $\rightarrow \text{cis-2}(\text{OMe})$. (4 POINTS)
- (vi) BOTH TRANSITION STATES $\rightarrow \text{trans-2}$ ARE BETWEEN ~~ENERGY~~ TRANSITION STATE $\rightarrow \text{cis-2}(\text{OMe})$ AND $\text{cis-2}(\text{NO}_2)$. (4 POINTS)
- d) BECAUSE THE TRANS-EPOXIDE PRODUCT IS LOWER IN ENERGY THAN THE CIS-, ITS FORMATION COULD BE FAVORED ON THERMODYNAMIC GROUNDS. YOU MIGHT DO A COUPLE OF EXPERIMENTS TO TEST THIS:

- MIX PURE CIS-EPOXIDE WITH $\frac{3}{m}$, AND SEE IF EPOXIDE ISOMERIZES TO TRANS-. FOR THERMODYNAMIC CONTROL, SYSTEM MUST EQUILIBRATE, AND THIS EXPT. WOULD TEST WHETHER CIS \rightarrow TRANS EQUILIBRATION OCCURS. (10 POINTS)
- ~~PREPARE~~ COOL THE REACTION DOWN AND SEE IF PREFERENCE SWITCHES TO CIS-. YES, IF THIS DID SWITCH IT WOULD INDICATE GOING FROM THERMODYNAMIC ~~TO~~ TO KINETIC CONTROL. BUT WHAT IF YOU COOLED AND NOTHING HAPPENED? THEN YOU WOULDN'T KNOW WHETHER IT WAS ~~THERMODYNAMIC~~ KINETIC ALL ALONG, OR WHETHER YOU JUST HADN'T COOLED ENOUGH. (7 POINTS)
- "TEMPERATURE" ALONE: (3 POINTS)
(w/o CIS \leftrightarrow TRANS SWITCH)
- "EQUILIBRIUM" ALONE: (3 POINTS)