T | H | I | N | G

Exam 3
Chem 12
May 02, 2011

Name That Thing on Donald Trump's Head

page **1** (20) _____
2 (20) _____
3 (35) _____
4 (30) _____

_____
total (100)

___
chk

Please don't doodle in this space...

1. (8 points) In the lab you determined the rate of the reaction of peroxydisulfate and iodide under various conditions by noting the time required for the appearance of the blue I_3^--starch complex. But this reaction occurs — and I_3^- is produced — as soon as you mix the reactants. Explain briefly why the blue color did not form instantly, and how you were able to get rate information by measuring the time required for the color to appear. (Neither specific chemical formulas nor mathematical equations are required to answer this question.)

The presence of a carefully measured amount of $S_2O_3^{2-}$, which reacted with the initial I_3^-, delayed the onset of the blue color. The color signaled the time required for a specific amount of reactant(s) to be consumed & thus provided an approximate initial rate.

2. (12 points) One of the main concerns associated with nuclear reactor accidents like the recent one at Fukushima Daiichi is the release of radioactive iodide, $^{131}I^-$. This isotope decays in a first-order process with a half-life of 192.5 hrs. $\times \frac{3600\ sec}{1\ hr} = 6.930 \times 10^5\ sec$

(a) Calculate the rate constant for the decay process (in the customary units of sec^{-1}).

5

$$k = \frac{\ln 2}{t_{1/2}} = 1.000 \times 10^{-6}\ sec^{-1}$$

(b) How many days are required for the initial amount of $^{131}I^-$ to decrease by 99.9%?

7

$$\ln\left(\frac{[^{131}I^-]_0}{[^{131}I^-]}\right) = kt \quad \Rightarrow \quad t = 6.906 \times 10^6\ sec$$

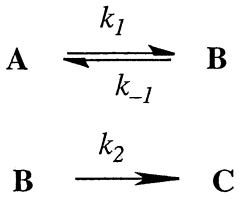
$\uparrow \frac{1}{0.001}$

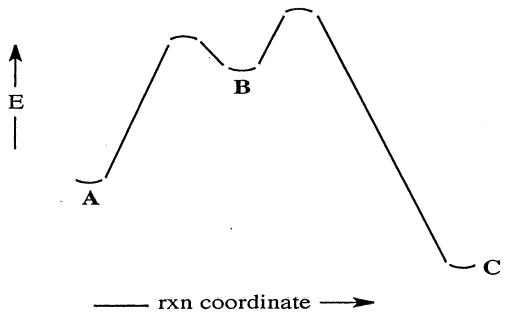
$= 1918\ hrs = 79.93\ days$

— so 0.1% remaining, or 0.001

20

3. (20 points) Consider a simple 2-step reaction mechanism, whose reaction coordinate diagram is shown at right.





2 (a) Which elementary mechanistic step has the largest activation energy? step 1

2 (b) Which mechanistic step is rate-limiting? step 2 (This has the highest-E t.s.)

(c) Show that applying the equilibrium approximation to the first step leads to the following rate law:

$$d[C]/dt = \frac{k_1 k_2}{k_{-1}}[A]$$

5 step-1 equilib —

$k_1[A] = k_{-1}[B]$

$\frac{d[C]}{dt} = k_2[B]$ $\qquad [B] = \frac{k_1[A]}{k_{-1}}$

$\Rightarrow \frac{d[C]}{dt} = \frac{k_1 k_2 [A]}{k_{-1}}$

(d) Experimentally, the reaction displays first-order kinetics, with a rate constant k_{obs}. What is the relationship between k_{obs} and the rate constants for the elementary mechanistic steps?

2 $k_{obs} = \frac{k_1 k_2}{k_{-1}}$

(e) Use your result from part d to find the relationship between the E_as for the individual mechanistic steps and the *observed* E_a for the overall reaction.

6 $A_{obs} e^{-\bar{E}_a(obs)/RT} = \frac{A_1 A_2}{A_{-1}} \frac{e^{-\bar{E}_a(1)/RT} e^{-\bar{E}_a(2)/RT}}{e^{-\bar{E}_a(-1)/RT}}$

$= \frac{A_1 A_2}{A_{-1}} e^{-(\bar{E}_a(1) + \bar{E}_a(2) - \bar{E}_a(-1))/RT}$

So $\bar{E}_a(obs) = \bar{E}_a(1) - \bar{E}_a(-1) + \bar{E}_a(2)$ seems reasonable, eh?

(f) Assume the overall reaction from A to C is exothermic by 50 kJ/mol, and the observed activation energy is 85 kJ/mol. What is the E_a for the reverse reaction, C —> A?

3 135 kJ/mol !

20

4. (15 points) Rate constants for the gas-phase conversion of HI to H_2 and I_2, measured at two temperatures, are as follows:

① $k = 3.52 \times 10^{-7}\ M^{-1}sec^{-1}$ at 282 °C = 555 K
② $k = 9.76 \times 10^{-5}\ M^{-1}sec^{-1}$ at 372 °C = 645 K

(a) What is the activation energy for the reaction (in kJ/mol)?

8 easiest to divide 2 Arrhenius eqns ⇒

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ plug 'n' chug ⇒ $E_a = 186\ kJ/mol$

(b) What is the Arrhenius A value?

7 plug E_a, k, T into Arrhen eqn & solve for A —

$A = 10^{11.05}$ (1.13×10^{11})

5. (20 points) Anthracene absorbs UV light and then fluoresces on a 20-ns timescale. In other words, the excited state, Anth*, returns to the ground state "Anth" on a timescale of 2.0×10^{-8} sec.

(a) What is the rate constant for this process? $k = 1/\tau = 5.0 \times 10^7\ sec^{-1}$

3

(b) When there is oxygen dissolved in the solution, the interaction of O_2 molecules with the Anth* (*bimolecular* "quenching"), deactivates the Anth*. This decreases its lifetime, but the observed rate of loss of Anth* still follows clean *first*-order kinetics. Explain briefly why the rate of loss of Anth* is observed to be first-order rather than second-order (or something more complicated).

5 [Anth*] must be much smaller than $[O_2]$ (even though the $[O_2]$ is $< 10^{-2}$ M !), so the rxn follows pseudo-1st-order kinetics — rate = $\underbrace{k[O_2]}_{k_{obs}}[Anth^*]$ for quenching

(c) When one plots the apparent first-order rate constant for loss of Anth* vs $[O_2]$, the plot is linear, with a slope of $2.5 \times 10^{10}\ M^{-1}sec^{-1}$ and a y-intercept of $5.0 \times 10^7\ sec^{-1}$. What kinetic parameters do these values correspond to?

6 Anth* → (Anth, $k_f = 5.0 \times 10^7\ sec^{-1}$ / path a)
Anth* → (Anth, k_q / O_2 / path b)

$$rate = -\frac{d[Anth^*]}{dt} = \underbrace{(k_f + k_q[O_2])}_{k_{obs}}[Anth^*]$$

$$k_{obs} = k_f + k_q[O_2]$$

k_f: int = $5.0 \times 10^7\ sec^{-1}$; k_q: slope = $2.5 \times 10^{10}\ M^{-1}sec^{-1}$

(d) What is the observed first-order rate constant when $[O_2] = 1.72 \times 10^{-3}$ M?

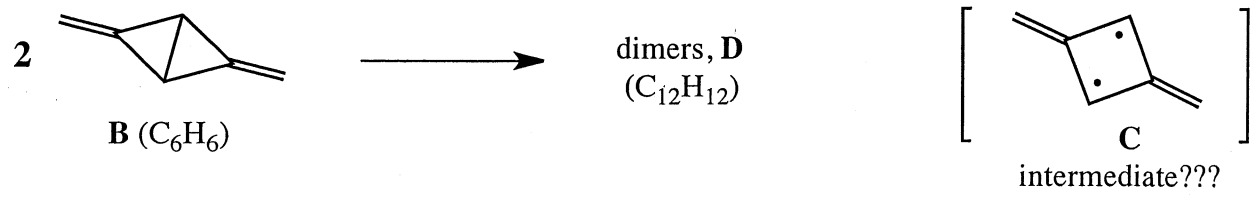
3 plug 'n' chug ⇒

$k_{obs} = 9.3 \times 10^7\ sec^{-1}$

(e) What is the timescale of the loss of Anth* under the conditions of part c (in sec and in ns)?

3 $\tau = 1/k = 1.08 \times 10^{-8}\ sec = 10.8\ ns$

6. (30 points) In solution, dimethylenebicyclobutane, **B**, dimerizes at temperatures above –80°C. That process may involve intermediate "biradical" **C**. Below are two possible mechanisms.



Mech 1: direct reaction of two molecules of **B**, i.e. **2B —> D**

and **Mech 2**: conversion of **B** to **C**, then reaction of **C** with another molecule of **B**, i.e.,

$$\mathbf{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{C}$$

$$\mathbf{B} + \mathbf{C} \xrightarrow{k_2} \mathbf{D}$$

(a) Write the relationship between the rate of loss of **B** and the rate of formation of dimer, **D**.

3 $$-\frac{1}{2}\frac{d[B]}{dt} = +\frac{d[D]}{dt}$$

(b) Write the differential rate equation implied by Mechanism 1.

3 $$\frac{d[D]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = k[B]^2 \quad \text{or} \quad -\frac{d[B]}{dt} = 2k[B]^2$$

(c) Use the steady state approximation to derive the differential rate equation implied by Mechanism 2.

$$\frac{d[D]}{dt} = k_2[B][C]$$

8 $$\frac{d[C]}{dt} = k_1[B] - k_{-1}[C] - k_2[B][C] = 0$$

$$[C] = \frac{k_1[B]}{k_{-1} + k_2[B]}$$

$$\frac{d[D]}{dt} = \frac{k_1 k_2 [B]^2}{k_{-1} + k_2[B]} \quad \text{or} \quad -\frac{d[B]}{dt} = \frac{2k_1 k_2 [B]^2}{k_{-1} + k_2[B]}$$

(d) The concentration of **B** was measured vs time, and the data are plotted in various ways on the following page. Some of the plots make sense, others don't. The best linear fit and the eqn of the line is given for each. *Circle the plot that tells you the order of the reaction* with respect to [**B**].

4

we obviously need a plot of $\ln[B]$ vs t or of $\frac{1}{[B]}$ vs t

(problem continues on next page...)

30

3

(e) What is the value of the observed rate constant?

In either case → slope = 2 k_{obs} so k_{obs} = 0.2857 $M^{-1}sec^{-1}$

(f) Which mechanism is consistent with your selection and why (briefly)?

5 Mech 1 is obviously 2nd-order

Mech 2 implies 2nd-order kinetics if $k_{-1} >> k_2[B]$

(g) The dimerization of **B** was found to have $\Delta H^{\ddagger}$ = 28.5 kJ/mol and $\Delta S^{\ddagger}$ = –117 J/molK. Which of the following statements is a reasonable interpretation of one or both values? (circle one or more)

4

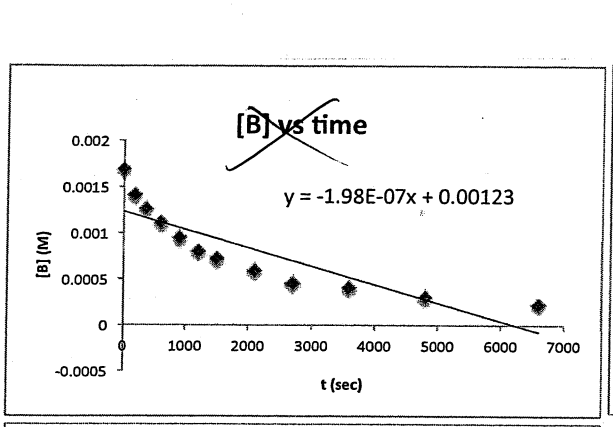
(i) The large $\Delta H^{\ddagger}$ indicates that the dimers (**D**) are less stable than **B**. - theme (ΔH° or ΔG°)

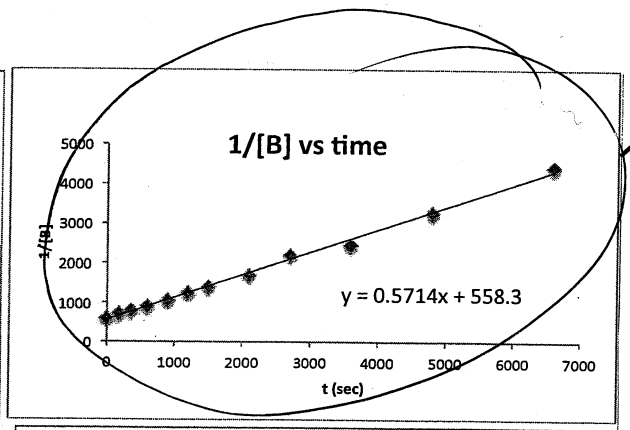
(ii) The negative $\Delta S^{\ddagger}$ implies that **B** probably forms **C** in the rate-limiting step. ?

(iii) The very negative $\Delta S^{\ddagger}$ implies that the reaction likely requires two species to collide with a very specific orientation in the rate-limiting step

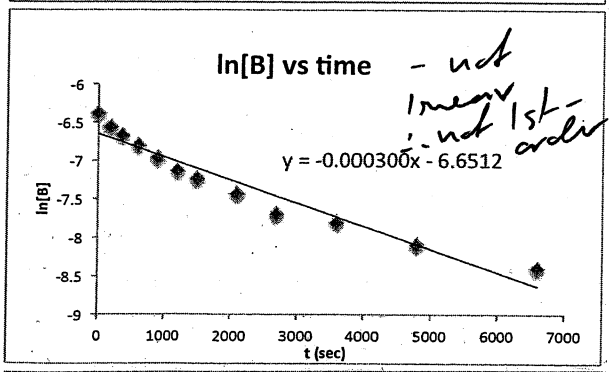
(iv) The positive $\Delta H^{\ddagger}$ implies that there is a significant increase in disorder when reactants go to the transition state ← pos $\Delta S^{\ddagger}$

(v) The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values indicate that the reaction is at equilibrium at about –30°C. eh ?

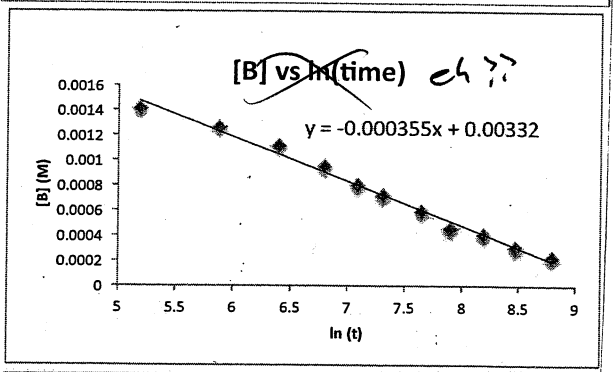




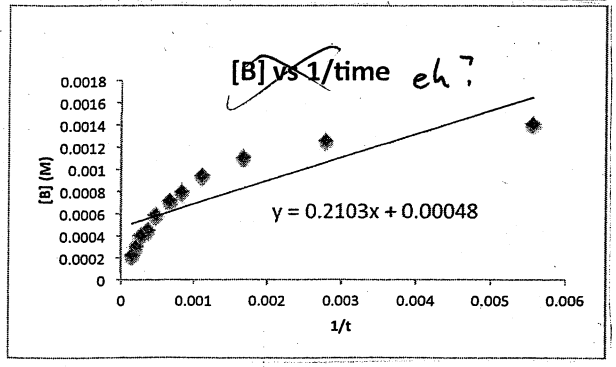
A Beautiful line!



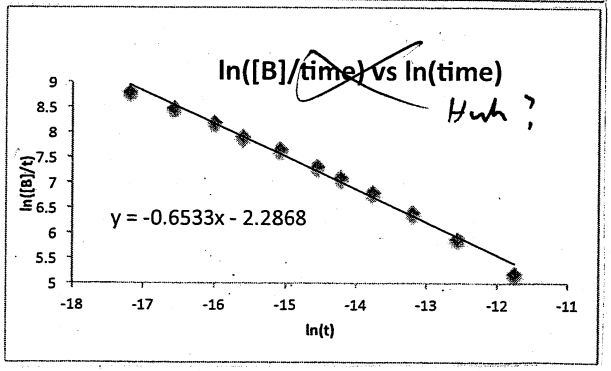
- not linear ∴ not 1st-order



eh ??



eh ?



Huh ?