Chem 12 HW set 10 – non-graded part

A. 48. see text

49. " "

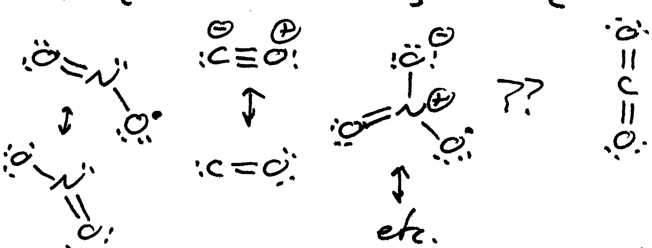
50. "Two" requirements? obviously the individual steps have to add to the overall (balanced) equation for the rxn. The mechanism must imply kinetic behavior that is consistent with experiment. In addition (+ beyond the scope of this chapter), all steps in a mechanism must be chemically reasonable based on what is already known about similar processes + intermediates. And, of course, every experimentally observable fact implied by the mechanism must be consistent with reality!
Even if all these criteria are satisfied, the mechanism is only "plausible", "possible", "likely", etc., not proven.
Very few rxns go via one-step mechanisms; most involve a series of steps.

51. see text

52. First step is rate-determining, so rate $= k[NO_2]^2$

overall rxn is $NO_2 + CO \rightarrow NO_3 + CO_2$

what are these structures??



etc.

(that's $NO_3$, not $NO_3^-$)

53. Overall rxn:

$tBu{-}Br + 2H_2O \longrightarrow tBu{-}OH + H_3O^+ + Br^-$

first step is rate-limiting, so rate $= k[tBu{-}Br]$

notice that the rxn produces acid – to measure the rate, an aliquot is removed, the rxn stopped, usually by cooling, + the acid is titrated with base.

$$\text{rate} = \frac{d[H_3O^+]}{dt} = -\frac{d(tBuBr)}{dt}$$

13\. 55. a. rate $= k[NO][O_2]$ — no

b. rate $= k_2[NO_3][NO]$  $[NO_3] = \frac{k_1[NO][O_2]}{k_{-1}}$ (equilib approx)

so rate $= \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2]$  that works

c. rate $= k[NO]^2$ — no

d. where's the $O_2$?! — notice that step 2 has a nitrogen turning into an oxygen! — this is just silly.

57\. Notice that step 4 is not an elementary step of the mechanism — that's a composite of a whole lot of steps that are all faster than the rate-limiting step 3. $HBrO_3$ & $H_2BrO_3^+$ are intermediates in steps 1-3

rate $= k_3[Br^-][H_2BrO_3^+]$

equilib approx: $[H_2BrO_3^+] = \frac{k_2[HBrO_3][H^+]}{k_{-2}}$

" " : $[HBrO_3] = \frac{k_1[BrO_3^-][H^+]}{k_{-1}}$

$$\text{rate} = \frac{k_1 k_2 k_3 [BrO_3^-][Br^-][H^+]^2}{k_{-1} k_{-2}}$$

59\. There's no reason to drop $[H_2O]$ just because it's constant — let's carry it along & deal with it later...

step 2 is rate-determining —

rate $= k_2[I^-][HOCl]$

equilib approx: $[HOCl] = \frac{k_1[ClO^-][H_2O]}{k_{-1}[HO^-]}$

$$\text{rate} = \underbrace{\frac{k_1 k_2 [H_2O]}{k_{-1}}}_{\text{const.}} \frac{[I^-][ClO^-]}{[HO^-]}$$

observed rate law: $k_{obs} = [I^-][ClO^-][HO^-]^{-1}$

62. Here, we don't know which step is rate-determining, so the equilibrium approximation is not appropriate.

$$O_3 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M$$

$$O + O_3 \xrightarrow{k_2} 2\,O_2$$

note that $O_2$ is formed on both steps & $O_3$ is lost in both steps

$O_2$ is formed twice as fast as step 2 happens!

$$\frac{d[O_2]}{dt} = \overset{①}{2k_2[O_3][O]} + \overset{②}{k_1[O_3][M]} - \overset{③}{k_{-1}[O_2][M][O]}$$

now we apply the steady-state approx to [O]

$$\frac{d[O]}{dt} = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O_3][O] = 0$$

$$[O] = \frac{k_1[O_3][M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

& plug this into the eqn above...

$$\frac{d[O_2]}{dt} = \frac{\overset{①}{2k_1k_2[O_3]^2[M]} - \overset{③}{k_1k_{-1}[O_2][O_3][M]^2}}{k_{-1}[O_2][M] + k_2[O_3]} + \overset{②}{k_1[O_3][M]}$$

sigh... last term above $\times \dfrac{k_{-1}[O_2][M] + k_2[O_3]}{k_{-1}[O_2][M] + k_2[O_3]}$ ---

$$= \frac{k_1k_{-1}[O_2][O_3][M]^2 + k_1k_2[O_3]^2[M]}{\text{denom.}}$$

now we combine terms – the ones circled cancel! Yea! The others add –

$$\frac{d[O_2]}{dt} = \frac{3k_1k_2[O_3]^2[M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

whew... (pant, gasp, pant...)

now, if step 1 is slow,

$k_2[O_3] \gg k_{-1}[O_2][M]$, so $\dfrac{d[O_2]}{dt} = 3k_1[O_3][M]$

This says that $O_2$ is produced at 3 × the rate of the first rxn — that rxn makes 1 $O_2$, then 2 more are "immediately" produced by the 2nd rxn.

If step 2 is slow,

$$k_{-1}[O_2][M] >> k_2[O_3], \text{ so}$$

$$\frac{d[O_2]}{dt} = \frac{3 k_1 k_2}{k_{-1}} \frac{[O_3]^2}{[O_2]}$$

63. $B \rightarrow E + F$

proposed "mechanism"

$$B + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B^* + B$$ — an exchange of energy such that $B^*$ now has enough energy to surmount the barrier. This "mechanism" made me wonder if the author had completely lost his mind... but there's a point that will be made in part c...

$$B^* \xrightarrow{k_2} E + F$$

a.

$$\frac{d[E]}{dt} = k_2[B^*]$$

$$\frac{d[B^*]}{dt} = 0, \text{ as usual...}$$

blah blah blah...

$$\text{rate} = \frac{k_1 k_2 [B]^2}{k_{-1}[B] + k_2}$$

b. Of course the rxn is first-order! Ok, we'll continue to play along... hmmm... if $k_2 >> k_{-1}[B]$, it would be 2nd-order; if $k_{-1}[B] >> k_2$, rxn is 1st-order, with rate $= \frac{k_1 k_2}{k_{-1}}[B]$

c. Exchange of energy among molecules, as shown explicitely in "step 1" of this "mechanism" is always super-fast — these collisional energy exchanges never show up in the kinetics, though they must always happen!

c. Sigh --- I should get HW points too ...

64. ok, that one's not bad - see text.

65. Some collisions have insufficient energy, & others occur in the wrong orientations. With flexible molecules, one or both reacting partners must be in the correct conformation ("shape") and the collision must occur at the right site with sufficient energy.

67. $2HI \rightarrow H_2 + I_2$ (another fascinating rxn)

$E_a = 186\ kJ/mol$ 555K $k = 3.52 \times 10^{-7} M^{-1}s^{-1}$

645K $k = ?$

You can solve this by using the $E_a$ + k at 555K to find the Arrhenius A-value, then calculate k at 645K. Or, take the ratio of 2 eqns -

$$\frac{k_1}{k_2} = \frac{A e^{-E_a/RT_1}}{A e^{-E_a/RT_2}}$$

$$\ln(k_1/k_2) = -E_a/RT_1 - -E_a/RT_2$$

(It's not essential to use logs here)

$$\ln(k_1/k_2) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$k_1 = 3.52 \times 10^{-7} M^{-1}s^{-1}$; $E_a$ = 186000 J/mol; $T_2$ = 645K; $T_1$ = 555K

$k_2 = 9.76 \times 10^{-5} M^{-1}s^{-1}$

70. Use the eqn above -

$$\ln(1/2) = \frac{E_a}{R}\left(\frac{1}{308K} - \frac{1}{298K}\right)$$

$E_a = 53\ kJ/mol$

If $E_a = 85\ kJ/mol$, $\ln(k_1/k_2) = \frac{85{,}000\ J/mol}{8.314\ J/mol\,K}\left(\frac{1}{308K} - \frac{1}{298K}\right)$

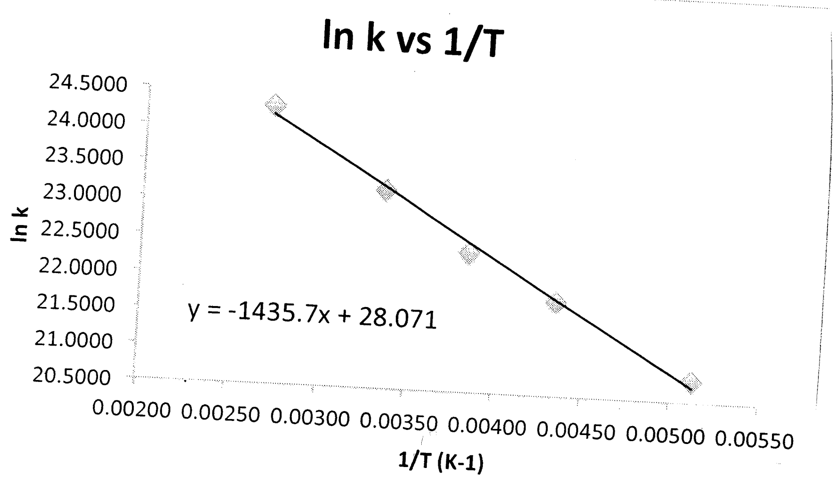
$k_1/k_2 = 0.33$ $k_2 = 3 \times k_1$ i.e. factor of 3 inc. in rate

73. $k = Ae^{-E_a/RT}$

$\ln k = \ln A - \frac{E_a}{RT}$ plot $\ln k$ vs $1/T$ —

slope $= -E_a/R$ ; intercept $= \ln A$

| T (K) | k (M-1 s-1) | 1/T | ln k |
|---|---|---|---|
| 195 | 1.08E+09 | 0.00513 | 20.8002 |
| 230 | 2.95E+09 | 0.00435 | 21.8051 |
| 260 | 5.42E+09 | 0.00385 | 22.4134 |
| 298 | 1.20E+10 | 0.00336 | 23.2082 |
| 369 | 3.55E+10 | 0.00271 | 24.2928 |




slope $= -1435.7$
$= -E_a/R$

$E_a = 11.9$ kJ/mol

int $= 28.071$
$= \ln A$

$A = 1.55 \times 10^{12}$

99. chirping freq $= 178$ min$^{-1}$ $= 2.97$ sec$^{-1}$ (2.97 Hz) at 298.2 K
$126$ min$^{-1}$ $= 2.10$ sec$^{-1}$ 293.5 K
$100$ min$^{-1}$ $= 1.67$ sec$^{-1}$ 290.5 K

plot of $\ln k$ vs $1/T$ is a beautiful line with slope
$= -6475.4$ ⇒ $E_a = 53.8$ kJ/mol
($A = 8.0 \times 10^9$)

b. $T = 15°C = 288.2$ K ⇒ $k = 1.42$ sec$^{-1}$ $= 85$ min$^{-1}$

c. !!! I think you just have to plug 'n' chug to do this.

100. Flash freq $= 1/16.3$ sec $= 0.0613$ s$^{-1}$ at 294.2 K
$= 1/13.0$ sec $= 0.0769$ s$^{-1}$ at 301.0 K

$E_a = 24.5$ kJ/mol at 30.0°C, $k = 0.0839$ s$^{-1}$ ⇒ $1/k = 11.9$ sec

c. plug 'n' chug.