

1. 54. Exercise 17 rate law was $k[\text{NO}]^2[\text{Cl}_2]$

$$(a) \text{ rate} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{Cl}_2]}{dt} = \frac{1}{2} \frac{d[\text{NOCl}]}{dt}$$

$$\text{rate} = k_2 [\text{NOCl}_2][\text{NO}]$$

$$\frac{d[\text{NOCl}_2]}{dt} = k_1 [\text{NO}][\text{Cl}_2] - k_{-1} [\text{NOCl}_2] - k_2 [\text{NOCl}_2][\text{NO}] = 0$$

$$[\text{NOCl}_2] = \frac{k_1 [\text{NO}][\text{Cl}_2]}{k_{-1} + k_2 [\text{NO}]}$$

$$\text{rate} = \frac{k_1 k_2 [\text{NO}]^2 [\text{Cl}_2]}{k_{-1} + k_2 [\text{NO}]}$$

if 1st step is rate-limiting (slow), $k_2 [\text{NO}] \gg k_{-1}$
 $\text{rate} = k_1 [\text{NO}][\text{Cl}_2]$

if 2nd step is " " " " $k_{-1} \gg k_2 [\text{NO}]$
 $\text{rate} = \frac{k_1 k_2 [\text{NO}]^2 [\text{Cl}_2]}{k_{-1}}$

this must be the case, as the experimental rate law is $k[\text{NO}]^2[\text{Cl}_2]$

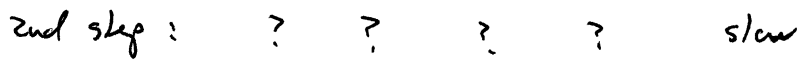
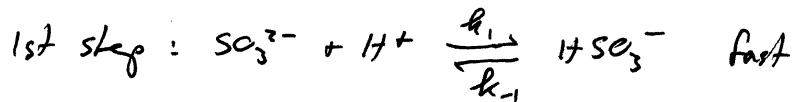
(b) If 1st step is slow, we can write $\text{rate} = k_1 [\text{NO}][\text{Cl}_2]$
 or square everything else

(c) If 2nd step is slow, we can use the equilib approx,
 $[\text{NOCl}_2] = \frac{k_1 [\text{NO}][\text{Cl}_2]}{k_{-1}}$

$$\text{so rate} = \frac{k_1 k_2 [\text{NO}]^2 [\text{Cl}_2]}{k_{-1}}$$

(d) Both results are identical to those obtained in part a.

2. 58. rate = $k[\text{BrO}_3^-][\text{SO}_3^{2-}][\text{H}^+]$



subsequent steps irrelevant

In step 2, HSO_3^- must react, so rate = $k_2[\text{HSO}_3^-][?][?]$

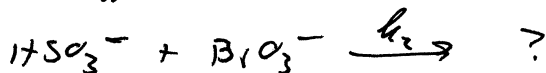
If step 1 is a rapid equilibrium,

$$[\text{HSO}_3^-] = \frac{k_1[\text{SO}_3^{2-}][\text{H}^+]}{k_{-1}}$$

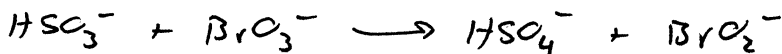
so rate = $\frac{k_1 k_2}{k_{-1}} [\text{SO}_3^{2-}][\text{H}^+][?][?]$

comparison with the observed rate law indicates that only $[\text{BrO}_3^-]$ is missing

so step 2 must be



the products are $\text{Br}^- + \text{SO}_4^{2-}$, so the BrO_3^- must eventually lose all its oxygens (Br goes from +5 to -1 ox state) + HSO_3^- 's sulfur must gain one — how about

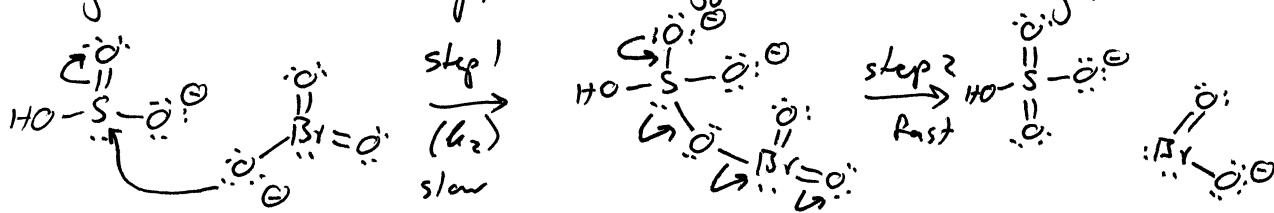


There may be other reasonable possibilities for the products of this step

this could lose H^+ to make SO_4^{2-}

this would then give up another O, then another

I don't see how an O can be transferred like that in a single mechanistic step, so I'll suggest the following:



3. 60. (a) rate = $\frac{d[\text{COCl}_2]}{dt} = k_3 [\text{COCl}] [\text{Cl}_2]$ need 2 equilib approximations

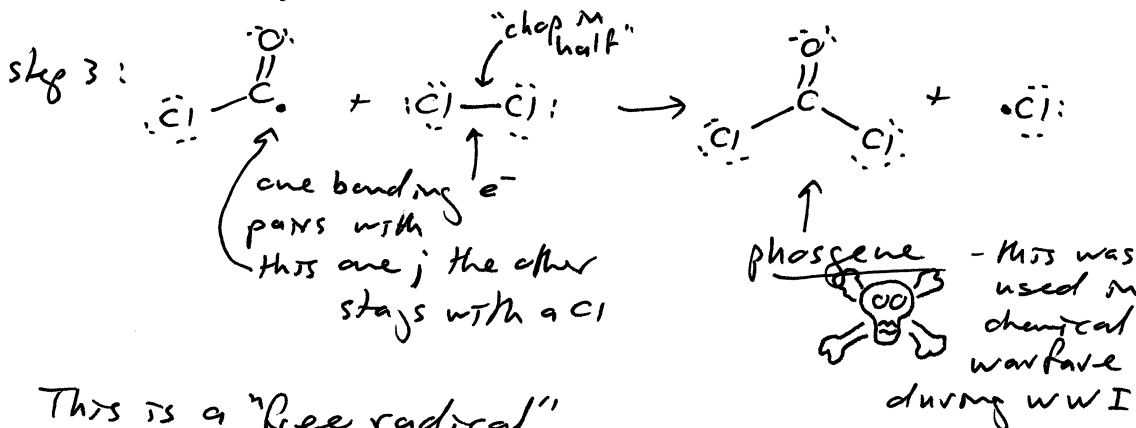
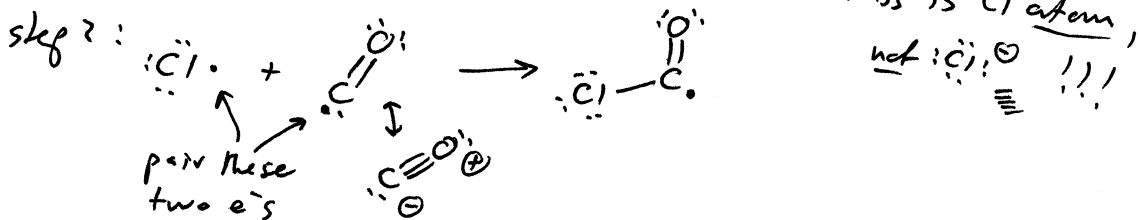
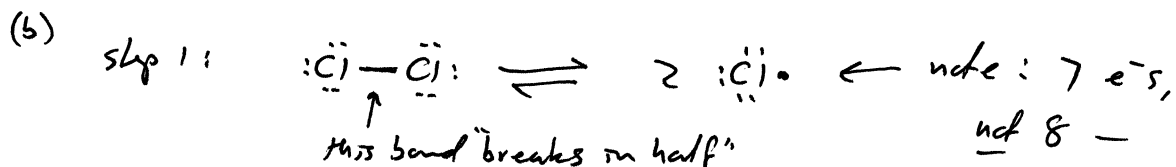
$$[\text{COCl}] = \frac{k_2 [\text{Cl}] [\text{CO}]}{k_{-2}} + [\text{Cl}] = \frac{k_1^{1/2} [\text{Cl}_2]^{1/2}}{k_{-1}^{1/2}}$$

$$\text{rate} = \frac{k_1^{1/2} k_2 k_3}{k_{-1}^{1/2} k_{-2}} [\text{Cl}_2]^{3/2} [\text{CO}]$$

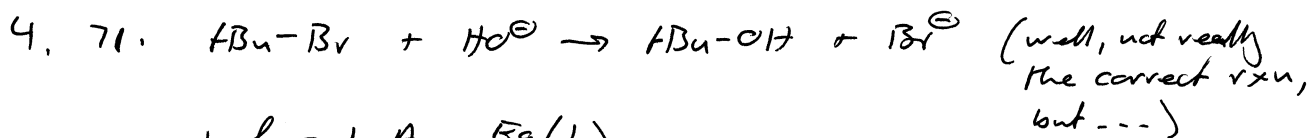
$$k_1 [\text{Cl}_2] = k_{-1} [\text{Cl}]^2$$

wow!

Cl + COCl are intermediates - that's why we expressed their concentrations in terms of equilibria with other things!



This is a "free radical" chain rxn - notice that the Cl· from step 3 can react with CO + repeat step 2 - steps 2+3 continue thousands of times before 2 radicals - species with unpaired e⁻s - collide + bond, stepping the chain.



$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

plot of $\ln k$ vs $1/T$ is linear with slope = -11,000
+ intercept = 33.5

a. $-11,000 = -E_a/R$

$$E_a = 91.5 \text{ kJ/mol}$$

b. $33.5 = \ln A$

$$A = 3.5 \times 10^{14}$$

c. plug in slope, int, + T
or use Arrhenius eqn

$$k = 0.0330 \text{ sec}^{-1}$$

72. plot $\ln k$ vs $1/T \Rightarrow$

$$\text{slope} = -E_a/R = -12447$$

$$E_a = 103 \text{ kJ/mol}$$

$$\text{int} = \ln A = 31.52$$

$$A = 4.9 \times 10^{13}$$

5. 68. we could plot $\ln k$ vs $1/T$ here, or ...

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

plug in k_2 + T_2 ... $E_a = 208 \text{ kJ/mol}$

To find k at 598K (325°C), plug in E_a , k_1 , + T (from above)

+ the new T + solve for the new k -

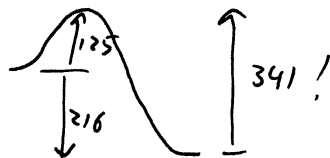
I get $1.4 \times 10^{-5} \text{ s}^{-1}$ (note that this is slower than the 660K rate by a factor of ~50 - seems about right)

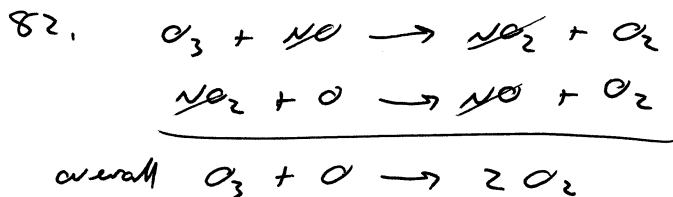
If initial pressure is 894 torr, after 1 half-life, $P = 447$ torr, after another, $P = 223.5$ torr, and after a 3rd, $P = 112$ torr

i.e. $1/8$ or $1/2^3$ the initial P .

76. $\Delta G^\ddagger = -216 \text{ kJ/mol}$ + $E_a = 125 \text{ kJ/mol}$

E_a for reverse rxn is
341 kJ/mol





NO is the catalyst - it accepts an O from ozone in step 1 & delivers it to O atom in step 2 - NO is neither formed nor destroyed in the rxn (overall) (NO₂ is an intermediate)

$$\begin{array}{l}
 E_a(\text{uncatalyzed}) = 14.0 \text{ kJ/mol} \\
 E_a(\text{NO-catalyzed}) = 11.9 \text{ kJ/mol}
 \end{array}$$

$$\frac{k_1}{k_2} = e^{\frac{-(E_a(1) - E_a(2))}{RT}}$$

$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ 14.0 & 11.9 & \end{array}$
 watch the units!

you can call either rxn "1" or "2"; but be consistent!

$$\frac{k_1}{k_2} = 0.43 = \frac{1}{2.3}$$

$$83. \quad E_a(\text{Cl}_2\text{-catalyzed}) = 2.1 \text{ kJ/mol}$$

this rxn is 120 x as fast as the uncatalyzed. (at 298K)

This is why most freon use has now been discontinued.