CHEMISTRY 2C WORKSHOP U.C. DAVIS

REACTION MECHANISMS

Many reaction mechanism problems will ask you to derive a rate law that is both :

1.) representative of the overall reaction (NOT simply the rate-determining step)

AND

2.) free of all intermediate species (those substances which do NOT appear in the overall rxn)

In order to accomplish this feat, you must use a combination of rate constant expressions and equilibrium constant expressions.

Use the following example as a general format in solving for the rate law of a reaction mechanism.

EX. Determine the rate law for the following reaction mechanism :

Eq. 1	$Cl_2 \rightleftharpoons 2\ Cl$	(fast)
Eq. 2	$Cl + CHCl_3 \longrightarrow HCl + CCl_3$	(slow)
Eq. 3	$Cl + CCl_3 \rightleftharpoons CCl_4$	(fast)
overall	$Cl_2 + CHCl_3 \longrightarrow HCl + CCl_4$	

STEP 1 : Write a rate law for the slow step (rate-determining step) using reaction stoichiometry since all slow steps are elementary processes. This equation will serve as a sort of "skeleton" rate law which will be manipulated into one that satisfies our two opening conditions. → = Elem. Rxns.

$$rate = k_2 [Cl][CHCl_3]$$

STEP 2: Compare the reactants in the slow step rate law with the reactants in the overall reaction.

You should notice that [Cl] is an intermediate, for it does not appear in the overall reaction. Hence, your goal is to delete [Cl] from the slow step rate law in order to create a NEW rate law that is representative of the OVERALL reaction.

STEP 3: Use a fast equation that contains both the intermediate and the reactant that are found in the overall reaction. Use this equation to write an equilibrium constant expression.

From equation #1 $K_1 = k_1/k_{-1} = [Cl\cdot]^2/[Cl_2]$

STEP 4: Solve the equilibrium constant expression for the intermediate.

$[Cl\cdot] = ((k_1/k_{-1})[Cl_2])^{1/2} =$

$[Cl\cdot] = (k_1/k_{-1})^{1/2}([Cl_2])^{1/2}$

STEP 5: Substitute the value of [Cl·] determined in step 4 into the slow step rate law.

For Equation 2, the slow step, rate 2 $= k_2 [Cl\cdot][CHCl_3]$

$= k_2 (k_1/k_{-1})^{1/2}([Cl_2])^{1/2}[CHCl_3]$

Let $k_2 (k_1/k_{-1})^{1/2}$ = a new constant called k, and substitute this k into the above equation to get the overall rate law.

rate $= k([Cl_2])^{1/2}[CHCl_3]$

Now you have a rate law that satisfies both of the conditions outlined in the beginning of the handout.