

welcome to today's lecture on chemical kinetics
to remind you of what we did ah in the last class remember we were discussing elementary reactions

so elementary reactions are those which are characterized being single step in nature

and also going through a single transition state and then we try to differentiate an elementary reaction from a complex or composite reaction where we said that a composite reaction is made

up of a series of steps of elementary reactions after that we looked at the energy profile

the meaning of an energy profile both for an elementary and a sample complex reaction taking a specific example from there on we moved on to molecularity where

we said molecularity is nothing but the number of molecules based on the balanced chemical

equation that is taking part in a specific elementary reaction molecularity is only applicable

for elementary reactions please keep that in mind and for elementary reactions the other defining

feature is that molecularity which is the number of molecules taking part in that elementary

reaction is equal to the overall order of the reaction the difference being that molecularity

is a theoretical quantity which by looking at the balanced chemical equation we can determine

on the other hand order is an experimentally determined quantity ok and hence for elementary

reactions both molecularity and order are the same then in the last part of ah the previous

lecture we were talking about complex reactions how do you recognize or how do you realize that

the reaction you have in hands is complex or composite in nature

so one of the ways of doing it

is by detection of reaction intermediates as its written on this piece of paper well the moment

you have an intermediate what does what what does it mean that means it is at least having two

steps that means definitely more than one step and remember elementary reaction is a single

step nature

so if you have more than one step it definitely will tell you that it is a complex reaction ok then because it is having an intermediate one of the ways obviously of making

out whether this reaction is complex or not is to look at the presence or look for the presence

of an intermediate but do keep in mind that while there are intermediates which can be isolated

which can be easily looked at experimentally many intermediates are very short lived that

means they do not exist for a long enough time hence it might be very difficult for

us to actually look at an intermediate just by normal experimental means we

might have
to use advanced experimental methods to figure out whether the intermediate is
really existing
or not ok
so this was one of the ways of figuring out whether the reaction at hand is
complex or
composite in nature that is by the identification or the existence of a
reaction intermediate
the second way of doing it is by looking at the form of the experimental rate
equation which
is written at the top
so what we are saying is you look at the form of the experimental rate
equation that's what you are looking at and then we showed this example
so what is this example so
this example is the reaction between hypochlorite ClO^- and iodide I^-
in aqueous phases
giving as products chloride and hypiodite if the reaction had been elementary
so suppose
nothing is told to you about the reaction right nothing is told to you you
know you look
at this reaction to you it seems like like simple enough reaction right and
you can say
that ok then the rate should be just like as written out here r is equal to k
times the
concentration of ClO^- times the concentration of I^- now if this were
an elementary reaction
that means if this reaction really was single step in nature then this rate
law is perfectly
valid why because remember by the definition of elementary reaction I can just
by looking at the
balanced chemical equation write down the rate law right also look at the
molecularity one molecule
of ClO^- one molecule of iodide and look at
so I should not be saying one
molecule but anyway
so now if you go to rate the overall molecularity that is one plus one is
equal
to the or the molecularity which is one of ClO^- and one of I^- is
equal to the overall
order which is one plus one equal to two
so this is how you characterize an elementary reaction
hence again if this reaction was really elementary I could have said that k
our rate is equal to k
times ClO^- times I^- the concentrations of these now remember this
is a theoretical one
that means if this reaction had been elementary I can write in this form now
let us do an experiment
and try to figure out what the experimental rate law is in the real world
so then after
doing the experimentation this is what we get
so the rate law is actually or the rate
expression is actually given by this equation where r the rate is equal to k
the rate
constant times the concentration of ClO^- the concentration of I^-

over the concentration of o_h minus now what you immediately realize is if this had been elementary then this is what you had said in the last piece of paper but now you see there is o_h minus coming in o_h minus did not figure in the stoichiometry of our reaction so this immediately tells you this immediately tells you that the reaction is composite or complex in nature so that is why the name of this section or this part how you determine whether a reaction is complex or not by looking at the form of this experimental rate equation so you had thought that if this were elementary this would be the rate law but then experimentally the rate law that was determined was this which is different from what you would expect if it were an elementary reaction hence the reaction is composite or complex in nature so because this o_h minus which is coming in this rate equation was nowhere there in the stoichiometry of the equation now let us take another example say for example so we have this equation $2C_2 + H_2 \text{ (gas)} \rightarrow 2Cu + 2H_2$ giving you $2Cu + 2H_2$ equals now the observed rate law the experimentally observed rate law so the experimentally observed rate law is given like this $r = k [C_2]^2 [H_2] / k'$ where k, k', k'' are all constants right now this is the experimentally observed so remember this rate law is the one which we have observed experimentally so this expression is obtained from carrying out experiments now had the reaction been elementary right had the reaction elementary what would the or what would the rate expression be so the rate expression had it been elementary can be written as $r = k [C_2]^2 [H_2]$ so now look at this equation so $r = k'' [C_2]^2 [H_2]$ had the reaction will elementary right so we can write this rate expression straight away from the balanced chemical equation so this is I can say that had the reaction been elementary so had the reaction been an elementary reaction but clearly it is not so why because the observed rate law again the observed rate law which is this the observed rate law which is this is clearly different from the one you would have expected had the reaction been elementary in nature so again the form of the rate expression tells you immediately whether the reaction is elementary

or not because elementary reactions the rate law or the rate expressions can be written directly from the balanced chemical equation however when you do experiments you might end up having a different rate law and if the rate law is different from the one you are expecting from being in elementary reaction then you immediately understand immediately understand that this is a composite reaction so now you can say then the reaction is a composite reaction or one having a complex mechanism now suppose let us you know let us take another or let us have another way of looking at it since you are dealing with an elementary reaction and you have written the rate law based on your thought that this reaction might be an elementary one what would tell you from this rate law if the reaction had been elementary one that this actually might not be an elementary reaction this is a composite reaction i will reframe my question right let me repeat my question again probably i was not clear what i wanted to say was that looking at this rate law which you have written down or the rate expression which you have written down by supposing that the reaction went in an elementary form that is through single step single transition step would you be right or would you be correct in writing this elementary reaction your your initial thought would be no and this is the reason why so remember in elementary reaction molecularity and overall order are the same ok ok now going back to this equation how many molecules are you talking about two CO_2 two plus or how many species two of CO_2 two plus and one of H_2 so that means had the reaction been an elementary one had the reaction been an elementary one i would have said that this is a term molecular reaction where i have two species of CO_2 plus reacting with one of H_2 but see unimolecular reactions are ok because i have only one molecule bimolecular reactions are still ok because i have two molecules which have to collide simultaneously but think about a term molecular reaction above for us it is very hard to imagine that at the same time all the three molecules will collide to give rise to your product which means if this had been a single step reaction if this had been a single step reaction then three species one CO_2 plus another CO_2 plus and H_2 all these three all these three would have to collide simultaneously would have to collide simultaneously so that the reaction is single step in nature and the moment the reaction is single step it means its an elementary reaction but for term molecular reactions and above it is very difficult to have all the three species or all the three molecules collide at the same

time it is not that
 thermonuclear reactions do not exist yes they do exist but then you hopefully
 you understand by now
 that for unimolecular reaction we have collisions between the same molecules
 for bimolecular
 reactions we have collisions between two molecules have to collide at the same
 time for a single
 step reaction for the reaction being elementary while we go for term molecular
 higher molecular
 reactions it is very difficult to conceive the fact that all the three
 molecules will be coming
 together and colliding at the same time hence the probability the probability
 of term molecular
 reactions and above that means the probability of three molecules or more
 colliding at
 the same time to go through a single step reaction give rise to your products
 decreases and hence just by looking at the form of this reaction just by
 looking
 at this reaction and just by thinking about the reaction in terms of an
 elementary
 rate law it gives you an idea or it gives you a hint that maybe without
 knowing
 anything even that may be the reaction is not elementary in nature there is a
 good
 chance that the reaction can be a composite or complex one involving multiple
 steps at
 least more than one step
 so again the rate law or the experimental determined rate
 expression gives you loads of information not only in terms of what or how the
 rate
 depends upon the respective concentrations but also tells you also tells you
 whether whether
 my reaction is supposed to be a single step one or it would rather take place
 in multiple steps
 so this is one of the best ways of figuring out whether the reaction you are
 considering or the
 one in your hands is composite or elementary in nature
 so please keep this in mind one was the
 detection of the reaction intermediates and the second one was by looking at
 the rate law
 now for example let us take another you know another thing another example
 so let's go for this example now we have already considered two examples
 so this would be a third example
 so third example is ah this equation $2\text{N}_2\text{O}_5 \rightarrow 4\text{N}_2 + \text{O}_2$ right giving you four n o
 two plus o two right now the experimental determinant rate
 law for this one goes like this r is equal to k times $[\text{N}_2\text{O}_5]^2$
 so this is this is experimental right but had had the reaction been elementary
 nature
 so r would have been equal to k in two o five raised to the bar two
 so that is the
 overall order two is equal to the molecularity of the reaction which we get
 from the balanced
 form of the equation
 so this is when we say that if it had been an elementary reaction which

immediately

tells you then that this reaction is a composite or complex reaction so like this many examples can be given but the idea was for you to be able to figure out

whether the reaction given in front of you is supposed to be a complex one that is involving

a series of elementary steps or is supposed to be a single step reaction which then it would

be referred to as an elementary reaction where the order of the reaction is equal

to the molecularity of the reaction ok now let us talk about something which is also very

fundamental to this reaction mechanism its called rate limiting step or rate determining step ok

so this concept again is a fundamental and central importance

in case of reaction mechanisms will soon figure out what we mean by this suppose we consider a series

of elementary reactions what are the reactions like say the reactions are a going to x this is an elementary reaction say

step one of a reaction and say this is the rate constant or you know the rate of this is r_1 is

equal to say this is the rate constant is k_1 k_1 times a next x goes to y the rate constant

for this transformation is k_2 and this reaction again being elementary is equal

to r_2 given as this and finally we have y going to p where p is the product this is k_3 and

so this

is r_1 this is r_2 this is r_3 we say this is k_3 times the concentration of y ok

so each

of these steps or each of these reactions is an elementary reaction now when i add these

up

so when i add these up when i add all these up you can see x and x would cancel out y and y would cancel out

so i will be left with the actual equation a going to t now this

is the question you are asking if this conversion from a to p or reaction from a going to

p is definitely composited in nature because it is constituted of three distinct elementary

reactions now each elementary reaction is given by the corresponding rate expression r_1 r_2 r_3

each elementary reaction a going to x x going to y y going to p they are having

different rates and even before that you realize that x and y are intermediates because

they finally do not appear in the balanced equation now as i was saying before each each of

these each of these

so let me write it here see each step has its own right each elementary reaction

that means each step each step being an elementary reaction has its own rate

so the next question that comes to mind is really if my composite reaction or my complex reaction mechanism is composed of three such elementary steps and each elementary step is having its own rate then what will my final rate equation be or you know rate of the equation $A \rightarrow P$ or the reaction $A \rightarrow P$ going to be depend upon it can depend upon $A \rightarrow X$ it can depend upon $X \rightarrow Y$ it can depend upon $Y \rightarrow P$ right

so the question again you are asking is if I am having a series of consecutive steps which leads to my final equation $A \rightarrow P$ how would I know how would I know on what my rate of this conversion from A to P will be based on why because suppose you are going to follow your reaction by looking at the product P right then the formation of product P is going to depend upon Y

so the formation of Y is going to depend upon X and the formation of X is going to depend upon A

so you know keeping this thing in mind if if you were trying to analyze the reaction by looking at the formation of the product P of P it would be difficult and complex why because the formation of P depends on Y now the formation of Y depends on the formation of X and the formation of X now depends on A right

so P depends upon Y you see P is depending upon Y then I said Y depends upon X see Y is not depending upon the

formation of X similarly X will depend upon how it is found from A hence t is depend upon Y which in turn is dependent on X which channel is dependent upon A this tells you that this is quite a complicated it's quite a complicated picture ok

so this you should be as complicated

so let me write it again this is quite a complicated picture but see you also know you also know that many rate laws or many rate expressions are quite simple quite simple then then the question is how do we decide on which step the rate of reaction will depend upon because in these three consecutive reactions which have their own rates you do not know how each of these contribute to the final equation which is $A \rightarrow P$ but that

as I said though it is complicated many rare expressions are quite simple for you to deal with thus there must be a proper way of deciding that ok this step may be step one or step two or step three will tell you or will finally determine the overall rate of this transformation of $A \rightarrow P$

so let's now think about this in a little ah different manner so how ah do we you know think about this suppose one day you have to go to a friends place from your house right and then you have to traverse a road you go

through a road say you are taking your car or you are going uh you're traveling in a bus or you're travelling in some other mode of communication mode of transport let's consider that this is your home right and say this is your friend zone right so you have to go from here to here now as it happens one of the ways or one of the parts will go like this suppose from here you have a very broad road ok then in between for some reason the road becomes very narrow for ah say a certain stretch say one or two kilometers and then again it widens up and your friends home is somewhere here ok so just take this as a sample road trip you are taking from your home to your friends house or friends place now see if you are starting from here since the road is wide enough in this stretch then you will see the cars will travel pretty fast right there will travel very fast but the problem is the moment they come to this this place the moment they come to this place here a different thing happens now the cars have to slow down why because initially the road was pretty wide broad the width of the road was big enough but that many cars could go side by side at a decent speed but the moment the road narrows out here the moment there are narrows out here see what happens you see it has become very narrow see at this stretch only cars in one line can go through after that again it starts widening out hence the cars can again maintain their speeds ok now lets think about this in terms of your chemical reaction suppose this is step one right suppose this is step one ok suppose this is step one this is step two and this is step three it is very visible from this example that in steps one and three the cars would be travelling at a very good speed say high speed but the moment you come to step two the moment you come to step two what has happened is the cars had to slow down they had to slow down they had no other option because there was no road the road available was very narrow so the total time they took that means the rate at which you could leave your home and go to and reach your friends place was not determined by steps one and two but it was determined by step ah sorry it was not determined by steps one and three but it was determined by step two because this is the part which was the slowest stretch in terms of travel from your home to your friends place so we say that if this you know if this is the slowest step then slowest i mean slowest step then this is also referred to as the rate determining step or rate limiting step the other way of looking at it is or you know the other commonly used word for this one is called a

bottle neck why is it called a bottleneck
so if you do not
look at this if you think about this with the bottom it looks like a bottle
isn't it so
in you know what happens in a bottle there is a white base cylindrical going
like this and
then at the top the bottle becomes narrow right
so you have a white base like this then the
bottle is a cylindrical and then out at the top it narrows down it tapers down
that is the
neck of the bottle and that is why it is called the bottle neck
so the bottle neck wherever you
face a bottleneck this bottleneck is a slow step right this bottleneck being
the slowest step
it determines at which rate you are going to go from this place to the other
place which is your
friends place or in terms of a chemical reaction if i have three distinct
steps steps one two and
three then the slowest step which in this case say step two would finally
determine which at
what rate the reaction would be moving from the reactant side to the product
side it does not
matter at all how fast steps one and three are it does not matter why because
these are very
fast anyway where do i face the bottleneck i face the bottleneck in step two
so wherever have your
bottleneck that means whichever step is the bottom leg that means whichever
step is the slowest step
in a series of consecutive steps would give me the rate of the reaction or the
rate of your road trip
in this case the other steps do not matter at all
so this is extremely important in terms of the
reaction mechanism because when you have again many many steps and you are
trying to figure
out what would the rate depend upon or what would the actual rate be then you
would soon
realize that because my rate depends upon the bottle next step that means the
step which is
the slowest one
so my rate expression my rate expression would also be determined by the
slowest
step and not by any of the other steps which are faster than this slower one
ok
so hopefully
i have been able to impress upon you what our rate determining step means the
rate remaining
step is the one which poses the bottleneck the bottleneck is the place where
the rate is the
slowest and because the rate is sliced out here this is the one i repeat this
is the one which
determines the final rate of your reaction going from a to p
so this is extremely important
to remember right
so now going back to our series of ah you know elementary steps here say

if i go back to the series of elementary steps right i do not know now which one is the determining step now suppose i tell you that fine let the rate determining step be the first one let the rate determining step be the first one if the rate determining step is the first one in the series of reactions then it immediately falls out that for the series of reactions finally a going to p that means i have a going to p which is made up of these three elementary steps then the rate is equal to k_1 times concentration of a because because the step a going to x was the slowest step or the rate determining step and let me also write this here it does not matter how fast it does not matter how fast the other steps are so step one of the reaction is the slowest one the other two are faster than this hence the rate of the reaction is decided by this step only the other two steps do not matter at all i hope been able to make myself clear in terms of what would finally determine the rate of a reaction especially in case of a multi step process or a complex reaction as written out here and again i can then write if if the first step is the rate determining step sorry determining if the first step is the rate determining step then then the rate of the overall reaction will only depend on the first step so this is important if if the first step is the rate determining step ok then the rate of reaction will only depend on the first step the other two steps in this case no matter how fast they are will not matter at all so as usual lets take an example so let us have this three ClO^- going to ClO_3^- equals phase plus two Cl^- aqueous ok that the proposed the proposed reaction mechanism goes like this goes like this that $\text{ClO}^- + \text{ClO}^- \rightleftharpoons \text{ClO}_2^- + \text{Cl}^-$ then $\text{ClO}_2^- + \text{ClO}^- \rightarrow \text{ClO}_3^- + \text{Cl}^-$ minus ok again you cross check ClO_2^- is intermediate so if you add these two reactions you should be given getting back the balanced chemical equation right so this is the proposed reaction mechanism right so this what is very important this is the proposed reaction mechanics if step one is right limiting that means this is step one if step one is rate limiting ok then i can write for step one being the rate limiting step or the rate determining step so this was step one then r would be $k_1 [\text{ClO}^-]^2$ or r is $k_1 [\text{ClO}^-]^2$ ok if the first step is the rate limiting one now indeed indeed the experimentally observed one so r experimental is equal to $k_1 [\text{ClO}^-]^2$

so what does this tell you
so what it

tells you that whatever equation we observed experimentally and the proposed reaction mechanism

the reaction mechanism is a plausible one because why is it plausible the reaction mechanism is plausible or the proposed means its plausible

so i can say this a plausible reaction mechanism why do we say
so because if this was if

you know this what the rate limiting step if this was the rate limiting step then the r

would have been predicted to be k times $[NO]^2$ square right this being in elementary step overall

order is equal to the molecule or the reaction also from experiment we get the same rate

expression hence i repeat hence the word plausible that means whatever reaction mechanism is

plausible because the rate expression we predict from the steps of the reaction mechanism does

follow the one which is observed experimentally as given here let us do another

example real quick since we are on this $2NO_2(g) + F_2(g)$

gas gives me $2NO_2F(g)$ gas right ok experimentally experimentally so

let me write $r_{\text{experimental}}$ is $k [NO_2]^2$ concentration of F_2 so

this is $r_{\text{experimental}}$ right now what about the proposed reaction mechanism

so the proposed mechanism goes like this $NO_2 + F_2$ gives me NO_2

plus F then $NO_2 + F$ gives me NO_2F i should be writing another F out here

so there

are two steps to this reaction the first step is $NO_2 + F_2$ giving me $NO_2F + F$ then

$NO_2 + F$ giving me NO_2F the first check is you add these two up you add these two up

what you see is you get $2NO_2 + F_2$ giving you $2NO_2F$ right

so hence when i add

this up i get back the balanced chemical equation now you are also the proposed mechanism

you are saying that this is the slow step

so if this is a slow step if this is a slow

step then you immediately realize i can write r is equal to k times $[NO_2]^2$

and the moment i have written that i see

that this form does agree with the one observed experimentally hence the proposed mechanism

is a plausible one

so i can say this one is a plausible

so this one is a plausible plausible mechanism ok just because of the fact that my predicted rate expression based on the proposed mechanism does agree with

that observed experimentally

so this is important now one of the characteristic features you

have seen out here is for this reaction or even as a matter of fact for the reaction we ah

did before which was this one which was this one the first step the first step

was
the slow step
so this one was a slow step
so the first step was the slow step
for this reaction and for this reaction again the first step was the slow step
now just to
give an example you do not have to worry about it would you have all reactions
where ah the first
step is or do all reactions have the first step is a slow step not necessarily
right you know
reactions are complicated nature there are so many reactions out there and
there will be many
reactions where the first will not be the slow step now what do we do in that
case or you know
can we look at that in a different way how do we write the rate law
so let us take an example
this for you is just to understand just for you to understand let us not go
into the details of it i
will write some of the things down but i will not explain everything ah you
know which you will soon
see but this is for you to understand what happens if the first step is not
the determining step
as we have been doing out here right
so let us take an example like that ok so
here what we say is then that the first step is not rate determining the first
step is not rate determining
that is an example we are going to look at ok
so suppose i have this reaction $a + b \rightarrow \text{products}$ right and i am
told that a
proposed mechanism is as follows $a \rightarrow x$ right and then $b + x \rightarrow p$
now because the first step is not rate determining it immediately tells me that if
the first step is
not very determining and there are two steps then the second step has to be
determining right that
means a slow step right if that is the case then my proposed rate law becomes r
is equal to say if
this is ah ok if this is you know k_1 this is k_2 k_2 times concentration of b
times concentration
of x now this is absolutely fine right my second stage is my rate determining
step and i am what
i am writing is i am writing this in terms of the concentration of v_f
concentration of x see
what is the problem like the problem is here that the b is a reactant ok its a
reactant
good however what about x if you look at the two steps step one and step two
then a goes to
 x then $b + x \rightarrow p$ and then i sum it i get $a + b \rightarrow b$
so x does not appear
out there which means x is an intermediate now we have already discussed
before a bit
that all intermediates cannot be isolated all individuals are not easy to
handle and
cannot be easily observed experimentally hence it is better for us not to

write a rate expression involving an intermediate as much as possible we try to avoid any units in the final rate expression now how do we do that so what we do is we propose a mechanism such that this x does not feature in the rate expression and how do we do that so this is where I said I will not go into the details but I will just show you the example so that you have a better feeling of the same so what we say is that ok we will still go we will still go by this ok we will still go by this 2 steps a going to x and b plus a is going to be will make a slight change what is this change change changes as follows a goes to x and we give it an equilibrium sign so what we say is that this is k_1 this is k_{-1} and we call this the first step as a fast as a fast pre equilibrium step ok as a fast pre equilibrium step then obviously the next step is what $b + x$ going to b and this is k_2 and remember because this is the slow step or the rate determining step or the rate determining step which many books you will see right will write as r_d the rate determining step r_d then the rate law is $k_2 x$ as you had written in the previous slide but is there a way to replace x out is there a way to replace x out let us look at this a in equilibrium with x so what happens is at equilibrium if you look at step one right so if this is you know step one this is step two then I can write from step one which is a which is a in equilibrium with x first equilibrium k_1 and k_{-1} so what is k_1 k_1 is the rate constant for the forward reaction k_{-1} is the rate constant for the backward reaction at equilibrium remember we are considering step one here only at equilibrium what happens the rate of the forward reaction is equal to the rate of the backward reaction isn't it so what is the rate of the forward reaction so in both directions rates are elementary nature I mean these are elementary nature the reactions are ok so the rate of the forward reaction is k_1 times concentration of a and the rate of the backward reaction is equal to k_{-1} times concentration of x ok and because this is so you see we immediately have the expression of x or ah x written in terms of k_1 over k_{-1} into concentration of a now this is an extremely important step also also remember if this is an if this is an equilibrium situation if this is an equivalent situation then I am going to have an equilibrium constant

so the equivalent constant can be the big k the k equilibrium constant the k equilibrium constant from this one is what is equal to concentration of x over concentration of a right which is equal to k one over k minus one

so you see you have two forms two very interesting forms one is this and the second one is this now by doing this what you have done is if you go back to a rate determining step which determined my proposed rate law which is k two times b times x this x had to be replaced now based on this pre-equilibrium constitution what do I have I have x is equal to k one over k minus one into a then what I do is I take this and replace x by this expression that means now now my rate becomes so rate was k two times concentration of b times concentration of x now based on the fact that I have x is equal to this then I can write r is equal to k two times concentration of b now by concentration of x I replace k one over k minus one concentration of a or r is equal to then k two k one k minus one consideration of b concentration of a right so this is also k equilibrium right so then the other form is that r is equal to k two k equilibrium consideration of a concentration of b hence I gave you an example where the first step was not rate limiting some other subsequent step was and in that case if an intermediate is coming in then I assume something referred to as this fast pre-equilibrium and using that I replace I replace the intermediate by something which is in terms of reactant which you are which is more easy to handle for us which we can readily handle this I did not explain too much about fast pre-equilibrium but just to give you the flavor of what types of different complex reactions can come in different complications can come in one I can have a fast ah you know fast ah first step which is very determining in this case it is a second step that means in this case the second step but not the first step which is very determining and then it becomes more complicated and then say go on to give rise or you know go on to propose a different sort of rate or a different sort of mechanism right I hope I have been able to ah you know impress upon you the importance of this rate determining step and how reaction mechanisms plausible reaction mechanisms can be devised just some examples to ah you know to make sure that the proposed one is in agreement with the observed rate expression thank you