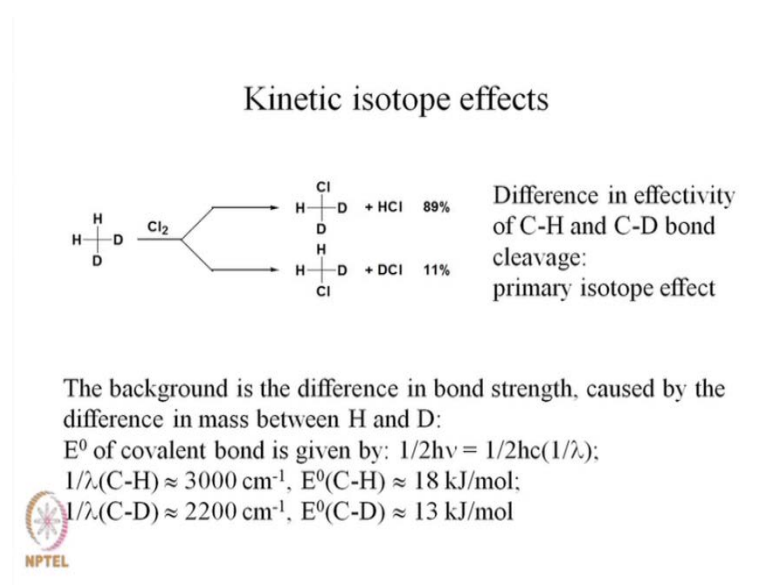


**Rate Processes**  
**Prof. M. Halder**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Module No. # 01**  
**Lecture No. # 20**  
**Kinetic Isotope Effects**

Hello, good morning everybody; so we were discussing rate processes.

(Refer Slide Time: 00:26)



So far we have talked about you know, like in last couple of lectures we have talked about these catalyzed reactions and in that case we discussed this acid base catalysis. Then, we discussed you know, general acid base catalysis; then, specific acid base catalysis; then, enzyme you know, when enzymes do general acid base catalysis; we also talked about then covalent catalysis. Then, you know, metal iron catalyzed reactions and there, we talked about also the mechanisms of such reactions. Now, the most important is that when we talk about this acid base catalysis then, protons are involved. Now, this proton means if you replace the proton which is involved in the reaction by a heavier atom like deuterium then what happens so that is a question.

So we now, talk on kinetic isotope effects. What is kinetic isotope effect? Now, so it is basically effect of isotope isotopic substitution on rate of chemical reaction so let us take the example of this  $\text{H}_2\text{C-H}_2\text{D}_2$  gas. So, let us look into the chlorination of this

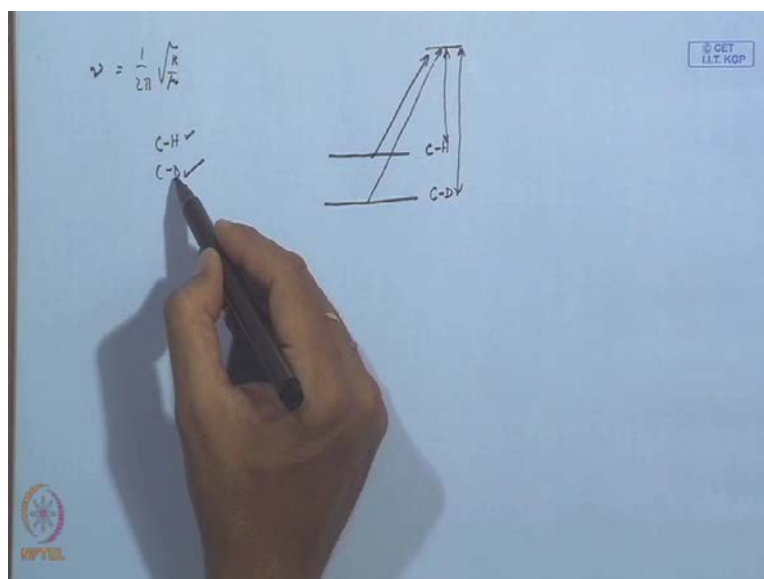
molecule. So, you know, it can do the reaction in these 2 possible pathways in one case. This hydrogen is replaced by chlorine in another case this deuterium is replaced by chlorine so in one case H C l is generated in the other case D C l is generated. You see that percentage of this mixture means, this mixture - this reaction mixture is basically a percentage of different percentages. I mean, hydrogen is replaced by chlorine to an extent of 89 percent and deuterium is replaced by chlorine to an extent of 11 percent. So, it is a huge difference you can see from the percentage yield of these two products so what could be the possible reason why this is happening. As I was telling that when it is the case of say acid base catalysis hydrogen is involved, so if you take say in place of a simple acid by a deuterated acid then, what will happen? So, these are the questions that may come in our mind.

That is why you know here we are taking a simple chlorination reaction. We see that there is a difference in affectivity; I mean, difference in the extent of reaction. So, the difference in affectivity of C-H and C-D bond cleavage; it looks like that C-H bond is easily cleaved than the C-D bond and that is the primary isotope effect because, these bond these particular bond is involved in the chemical reaction. So, if you replace this hydrogen I mean, this C-H bond by a C-D bond means here, what happened? You see that there is an enormous reduction in the percentage yield; so this isotopic substitution is has been made directly on to the reaction centre. Why is there a difference in affectivity? The background is the difference in bond strength caused by the difference in mass between hydrogen and deuterium difference in bond string does not necessarily mean that it is you know, chemical in chemical sense. It is basically in terms of you know, excitation when we when you do some chemical reaction it is you know, as per the absolute reaction rate theory that you have to put your reactant to the transition state. And, in the transition state out of the many vibrational modes, 1 mode has been converted to translational mode which is responsible for the rapture the bond.

That means the bond which requires more of activation will probably you know, do the reaction slow than compared to where you know, the bond requires you know, lesser amount of activation energy. Now, the ground state I mean the 0 energy for this particular bond. I mean, is it is given by  $\frac{1}{2} h \nu$  that is  $\frac{1}{2} h c$  by  $\lambda$ . So,  $\frac{1}{\lambda}$  by  $h c$  that is for your frequency for your C-H bond is 3000 centimetre inverse. You can get it from simply from higher spectra if you take higher spectra of a deuterated sample

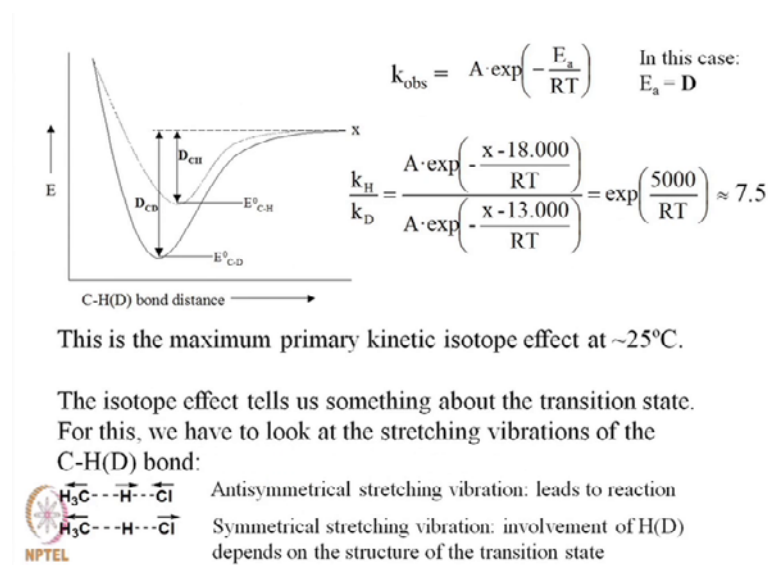
and another non-deuterated means hydrogenated sample of a given molecule where only difference is in the C-H bond is specific C-H bond. Then you will find that this C-H bond comes at a higher wave number than the carbon deuterium bond and the 0 energy for C-H is of the order of 18 kilo joule per mole compared to C-D which is 13 kilo joule per mole.

(Refer Slide Time: 07:34)



That means, if you have an energy level diagram, this is for your C-D and say this is for your C-H and suppose this is your transition state so what do you need you need to transfer this to here or may be this to here so it requires more of activation this is more compared to this one. Now, why is a, you know, wave number is - why the wave number for C-H is more because, you see that C-H and C-D. This one is heavier compared to this one. So, that means the reduced masses more for deuterium than for hydrogen. So, if you consider the Hooke's law then, the frequency  $\nu$  is equal to  $\frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  where  $\mu$  is the reduced mass. So, if force constant is remaining same or if you think that if you consider that there is no change in chemical bond strength, if you replace C-H by a C-D I mean, if you replace hydrogen by deuterium so only deciding factor is that this is because of you know, your difference in the mass of the concerned atom. Therefore, its frequency is less than this one. So, that expense why you know is it for C-H is more than for C-D which is 13 kilo joule per mole.

(Refer Slide Time: 09:21)

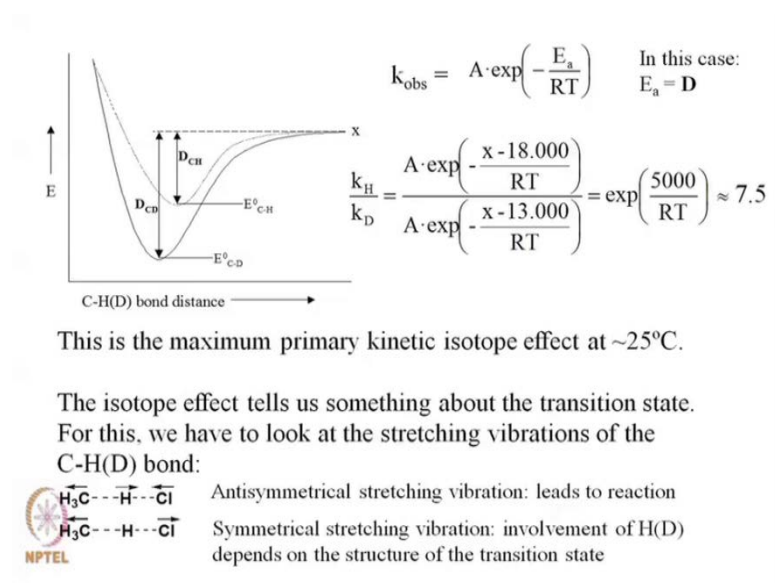


Now, it is the potential energy diagram if we look in to that this is bond distance if you plot energy as a function of bond distance. That is C-D bond distance; then, you will be seeing that it is the Morse type of potential. So, this dotted 1 is for C-H and the solid 1 is for C-D and this is your dissociation continuum. That is, if you can excite or if you can put your n symbol of molecules from here to here then, these corresponding bonds this C-D or C-H bonds will be ruptured because, this corresponds to you know, free C and free hydrogen. I mean, free C means this corresponds to rupture of these bonds. This is called the dissociation energy for C-H and this is your dissociation energy for you know, for your C-D and you see that is, it is not exactly at the at the bottom of your potential in the surface. It is a little above. This is because of the Heisenberg's uncertainty principle. So, observed rate is equal to a into E to the power minus E a by R T. So, this is your Arrhenius expression as I already have talked about may be in earlier lecture. In this case, E a is D basically the dissociation energy; so for when it is it is the case of hydrogen then it is you know, it is basically your 18 kilo joule and x is basically a factor; I mean it is it is a constant quantity that is x minus this much. This is also x minus this much. Therefore, you know, K H by K D is the rate constant ratio for hydrogen and deuterium hydrogen and deuterium; it comes out to be of the order of exponential to the power 5000 by R T which is of the order of 75.

So, this is the amount of activation that is required that is this much. This is also the amount of activation. This is the maximum primary kinetic isotope effect that one can

observe at 25 degree centigrade. That is at room temperature, why do we need to you know, consider such a discussion that? Because, the isotope effect can tell us something about the transition state and for this we have to look at the stretching vibration of C-H or C-D bond. Now, consider you know, C-H 3 H C I I mean the transition state of this shot; that is it is basically methane part and it is chlorine part and this is also a methane part and chlorine part so you know, this is an anti symmetrical stretching vibration and this is a symmetrical stretching vibration involvement of H D depends on the structure of the transition. Now, if this anti symmetric stretching happens then, H and C I will come close and (C) go away. That may lead to the chemical reaction; that is why isotope effect is very important. That is study of isotope effect on reaction is very important in order to elucidate the mechanism of chemical reaction; I mean, it gives us the idea about the transition state.

(Refer Slide Time: 13:41)



Symmetrical stretching vibration involvement of H and or D depends on the structure of the transition state. So, H exactly if H exactly is at the middle, it is a symmetrical transition state. If it is you know, close to methane I mean C-H 3 it is the early transition state and if H is close to C I it is called the late transition state. If this is a symmetrical transition state then, kinetic isotope effect is maximum and if it is not in the middle isotope effect will be less. As I told you that maximum kinetic isotope effect you can expect a 25 degree centigrade is of the order of 75 so here you can expect here you can expect about 75 but, I mean K H by K D; but, not in these 2 cases. You see that you

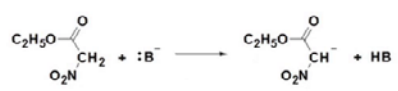
know, this is your reactant side; this is your product side so in the reactant side it is C-H bond product side it is H C l bond because you know, it is it is the reactant side and this is the product side in the same way it is C-H I mean C-H 3 D is the reactant side and D C l is the product side so since we are starting from this side to that that side. Therefore, it is important that I mean this much of difference if we can supply then the in simple can be promoted from here to this top of the hill and then, it will move on to the product side so you see that for your activation energy for the case when it is C-H bond it is less than it is than the case with C-D. Therefore, it requires more energy that means I mean if the activation energy is more . Therefore, the rate of reaction will be less. So, you can expect you know, a lot of difference in the rate and also the rate constant.

What about the early transition state? Early transition state means it resembles very close to you know, starting. So, you see that it is activation energy and this is your transition state and here this is the transition state. So, you see the activation energy is this much for your deuterium and this for your hydrogen. So, not much difference we can you know, expect here but, here the difference is huge. Whether it is early transition state or even if it is a late transition state you know, in that case your transition state where you know, this product, it is close to a product I mean, you see that hydrogen and chlorine these are very close and this is you know, length end. That means, you see that here E H and E D E a H activation energy for hydrogen and also activation energy for deuterium. So, this one is a little more than this one; in these 2 cases we can expect less than 75 that is you know, K H by K D is not exactly 75 because, in this case it is you know, the transition state is not exactly symmetrically disposed; I mean, hydrogen is not symmetrically disposed. So, these are the 3 situations I can think of with respect to C-H 3 H C l reaction.

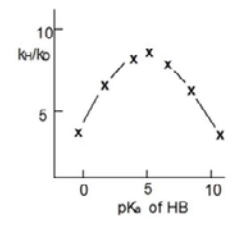
(Refer Slide Time: 17:42)


**Rule of thumb:**  
 $k_H/k_D \approx 4-7$ : bond cleavage, symmetrical transition state  
 $k_H/k_D \approx 1-4$ : bond cleavage, asymmetrical transition state;  
or no bond cleavage (secondary isotope effect)


**Example:**



Maximum isotope effect at symmetrical TS, so when  
 $pK_a(\text{acid}) = pK_a(\text{HB})$



$\text{:B}^- = \text{OH}^-, \text{H}_2\text{O}, \text{HCOO}^-, \text{CH}_3\text{COO}^-, \text{XC}_6\text{H}_5\text{O}^-,$   
, etc.

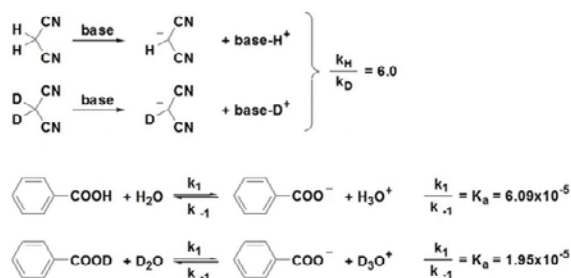


Rule of thumb: what is rule of thumb? Rule of thumb is that, if  $k_H/k_D$  is of the order is close to 4 to 7. Then, it is bond cleavage and it is it is nothing but, the anyhow it is symmetrical transition state of course, perfectly symmetrical transition state will give rise to  $k_H/k_D$  close to 7. So, a range from 4 to 7 corresponds to a symmetrical transition state. What about other case? Less than 4; so,  $k_H/k_D$  is 1 to 4. If it is in between 1 it is from 1 to 4 then there is a bond cleavage but, it is in asymmetrical transition state as like this one. This is symmetrical transition state but, this is not the symmetrical transition these 2 are not symmetrical transition state. It is either early or it is late or in that case, no real bond cleavage it is called the secondary isotope effect that is you know, at the reaction centre no bond cleavage but, you may expect a difference in rate for hydrogen for deuterium so it is it is called you know, a secondary kinetic isotope effect not the primary one as an example we can have this molecule which when reacting with base producing HB. Now, maximum isotope effect at symmetrical transition state when  $pK_a$  of the acid and  $pK_a$  of HB. These 2 are close or identical in that case you will be expecting because, in that case if these 2 are same that means the hydrogen will have the equal probability to be with this B or to be with the starting product so when  $pK_a$  acid is equal to  $pK_a$  HB then you can expect this one so you see that  $pK_a$  if you plot  $k_H/k_D$  for HB you see that and B is basically this you know,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{XC}_6\text{H}_5\text{O}^-$  so on. Then, you can will be seeing that it maximizes at 5 that means when  $pK_a$  of HB matches with that of acid then it maximizes so that corresponds to a symmetrical transition state.

In that case you can expect you know, this kinetic isotope effect that is  $k_H$  by  $k_D$  close to 7 but, in all other cases it is less than because, in other case  $P K_a$  acid is not equal to  $P K_a$  of  $H B$ . So, it is it is an interesting observation and interesting you know, conclusion. So, this is basically the rule of thumb that if you find  $k_H$  by  $k_D$  in between I mean 4 to 7, it is your symmetry, corresponds to symmetrical transition state. Otherwise, if it is less than 4 in between 1 to 4, it must be unsymmetrical or maybe possibly, it is not a direct isotropic effect as it is not a primary effect but, maybe it is you know, secondary kinetic isotropic effect.

(Refer Slide Time: 21:37)

Some more examples:



Some more examples that is C-H to C into in presence of base because there are 2 cyanide groups so these this carbon I mean this hydrogen will be these 2 hydrogen's will be very much acidic in presence of a base this you know, proton will be snatched and if it is you know, deuterated base it is giving base D plus. So, it has here it is found that  $k_H$  by  $k_D$  is 6 that is close to close to 7 that means we can expect a you know, symmetrical transition state and the best option will be  $P K_a$  and  $P K_a$  I mean these 2  $P K_a$  acid and  $P K_a$  of  $H B$  these 2 match. Then, possibly we are moving I mean, we are approaching  $k_H$  by  $k_D$  equal to 7 or may be 7.5. Another example that is a that is a rapid equilibrium that is  $H_2O$  giving rise to you know, it is a benzoic acid. So, benzoate and  $H_3O^+$  plus  $k_1$  by  $k_{-1}$ ; that is acid I mean  $K_a$  this acidity equilibrium it is 6 into ten to the power minus 5 and if it is deuterium then it is  $K_a$  is much less 2 into ten to the power minus 5 about 3 times more for hydrogen. So, I know this forward reaction possibly you know,

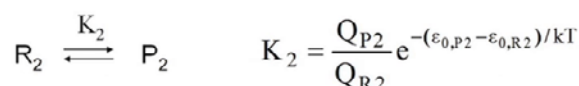
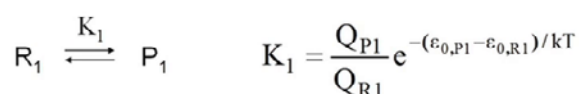


this upper one that is forward rate is more for this one compared to this forward rate because the because this detachment of O D bond it may be requires it it is requiring more you know, activation that is why this forward process is a little you know, less in rate wise.

(Refer Slide Time: 24:00)

## Isotope Effect Theory

### Equilibrium Isotope Effect



$$Q^{\text{tot}} = Q^{\text{tr}} Q^{\text{rot}} Q^{\text{vib}} Q^{\text{el}} \quad \epsilon_0^{\text{tot}} = \epsilon_0^{\text{el}} + \epsilon_0^{\text{vib}}$$

$$\text{Since } Q^{\text{el}} = 1: \quad Q^{\text{tot}} = Q^{\text{tr}} Q^{\text{rot}} Q^{\text{vib}}$$



Isotope effect theory: now, equilibrium isotope effect although we are talking about kinetics on kinetics but, let us look into equilibrium isotope effect you know, you know, quickly so this is reaction 1 product 1 so corresponding you know, using statistical mechanical concepts you know, equilibrium constant can be written in terms of the partition functions. In terms of partition function, we can write like this for your this is for E 0 product this is for your E 0 reactant in the same way for P 2 and R 2 where q total is translation. It is a combination of translation rotation vibration and electronic and total energy electronic plus vibration. Now, electronic partition function is taken to be 1. Therefore, total partition function q is translation it is it is the product of translation rotation and vibration.

(Refer Slide Time: 25:07)

$$Q^{\text{rot}} = \frac{8\pi^2(8\pi^3 ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma h^3} \quad Q^{\text{tr}} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V$$

$$Q^{\text{vib}} = \prod_i^{3n-6} (1 - e^{-h\nu_i/kT})^{-1} \quad \epsilon_0^{\text{vib}} = \sum_i^{3n-6} \frac{1}{2} h\nu_i$$

$$\therefore \frac{K_1}{K_2} = \frac{Q_{P1}Q_{R2}}{Q_{R1}Q_{P2}} e^{-(\epsilon_{0,P1} - \epsilon_{0,R1} - \epsilon_{0,P2} + \epsilon_{0,R2})/kT}$$

*Born-Oppenheimer Approximation:*



$$\epsilon_{0,P1}^{\text{cl}} - \epsilon_{0,R1}^{\text{cl}} = \epsilon_{0,P2}^{\text{cl}} - \epsilon_{0,R2}^{\text{cl}}$$

Now, the expression for q rotation is this rotational partition function so q translation is this and q vibration is this and you know, E 0 vibration is given by like this expression 0. vibrational energy . Therefore, K 1 by K 2 K 1 by K 2 that is you know, equilibrium constant for this one and this one that is K 1 by K 2 can be written in this way and also applying Bon Oppenheimer approximation, that electronic motion is much faster than your vibrational motion and vibrational motion is much faster than your rotational motion. So, in this way we can factorize the you know, total wave function into products from Bon Oppenheimer approximation we can have this relation.

(Refer Slide Time: 26:07)

$$Q^{\text{rot}} = \frac{8\pi^2(8\pi^3 ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma h^3} \quad Q^{\text{tr}} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V$$

$$Q^{\text{vib}} = \prod_i^{3n-6} (1 - e^{-h\nu_i/kT})^{-1} \quad \epsilon_0^{\text{vib}} = \sum_i^{3n-6} \frac{1}{2} h\nu_i$$

$$\therefore \frac{K_1}{K_2} = \frac{Q_{P1}Q_{R2}}{Q_{R1}Q_{P2}} e^{-(\epsilon_{0,P1} - \epsilon_{0,R1} - \epsilon_{0,P2} + \epsilon_{0,R2})/kT}$$

*Born-Oppenheimer Approximation:*



$$\epsilon_{0,P1}^{\text{cl}} - \epsilon_{0,R1}^{\text{cl}} = \epsilon_{0,P2}^{\text{cl}} - \epsilon_{0,R2}^{\text{cl}}$$

Substituting the respective expressions substituting partition function then, vibrational 0 energies to this K 1 by K 2 this one here.

(Refer Slide Time: 26:17)


Substituting partition functions and vibrational zero-point energies:

$$\therefore \frac{K_1}{K_2} = \frac{\sigma_{R1}\sigma_{P2}}{\sigma_{P1}\sigma_{R2}} \left( \frac{m_{P1}m_{R2}}{m_{R1}m_{P2}} \right)^{\frac{3}{2}} \left( \frac{A^{P1}B^{P1}C^{P1}A^{R2}B^{R2}C^{R2}}{A^{R1}B^{R1}C^{R1}A^{P2}B^{P2}C^{P2}} \right)^{\frac{1}{2}} \times$$

$$\underbrace{\frac{\sum_i^{3n-6} (1 - e^{-u_{i1}})/(1 - e^{-u_{i2}})}{\sum_l^{3n-6} (1 - e^{-u_{l1}})/(1 - e^{-u_{l2}})}}_{\text{EXC}} \times \underbrace{\frac{\exp\left\{\sum_i^{3n-6} (u_{i1} - u_{i2})/2\right\}}{\exp\left\{\sum_l^{3n-6} (u_{l1} - u_{l2})/2\right\}}}_{\text{ZPE}}$$

**MMI**

$u_i = h\nu_i/kT$       $i \equiv$  reactant index      $l \equiv$  product index



We can get 3 things; 1 is mass movement inertia part another is 0 energy term; another is excitation term where  $u_i$  is  $h\nu_i/kT$   $i$ -th vibrational you know, quantum or  $i$ -th mode is  $i$  is the reactant  $l$  is the product index.


(Refer Slide Time: 27:01)

$$\therefore \frac{K_1}{K_2} = \frac{\sigma_{R1}\sigma_{P2}}{\sigma_{P1}\sigma_{R2}} \cdot \text{MMI} \cdot \text{EXC} \cdot \text{ZPE}$$

MMI = isotope effects on translation and rotation.  
(Mass moment inertia term)

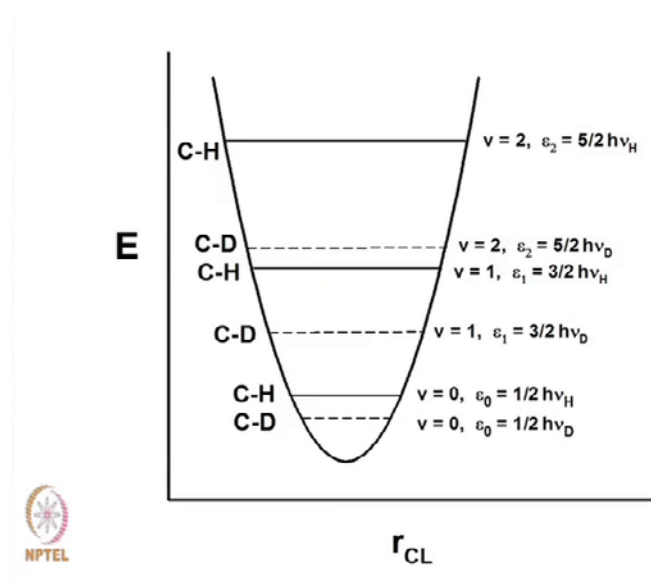
ZPE = isotope effects on  $\nu_i$  at 0 K. (zero point energy term)

EXC = isotope effects on population of vibrational excited states at T (density of vibrational states).  
(excitation term)



Therefore,  $K_1$  by  $K_2$  is basically your product of this mass moment inertia term excitation term and 0 energy term and of course, some other numbers.

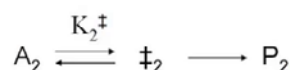
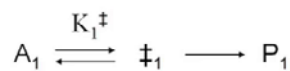
(Refer Slide Time: 27:20)



Now, let us look into this potential energy diagram for your C-H and C-D bond I mean, C-D vibration, C-H vibration and C-D vibration. You see that for C-D it is lower as I told you, if you look into the Hooke's law expression since deuterium is heavier compared to hydrogen. Therefore, you know,  $\nu$  is equal to  $1/2\pi\sqrt{K/\mu}$ . So,  $\mu$  is more means its corresponding frequency is less so 0 energy is less compared less for deuterium than for hydrogen so there is a difference you see there is a difference between this dotted and the solid line. So,  $\nu_H$  is more than  $\nu_D$  if you look into this expression it is more for deuterium. Therefore, this number will be less provided  $K$  is same for C-H and C-D. Of course, the chemical characteristic and the strength of a chemical bond should not depend on the mass; it depends on the electronic environment; **how to** electronic configuration?. Therefore, you know, for C-D you know,  $v$  is equal to 0 it is less it is even even difference is more when we are in the first vibrational quantum for C-H and C-D. It is still more for vibrational quantum 2 so this way this gap increases because you know, because the mass is is you know, for hydrogen it is 1 and for deuterium is 2 so it is increasing difference is increasing.

(Refer Slide Time: 29:15)

### Kinetic Isotope Effects



$$k_1 = \kappa_1 \frac{kT}{h} K_1^\ddagger = \kappa_1 \frac{kT}{h} \frac{Q_1^\ddagger}{Q_1} e^{(\epsilon_{0,1} - \epsilon_{0,1}^\ddagger)/kT}$$

$$k_2 = \kappa_2 \frac{kT}{h} K_2^\ddagger = \kappa_2 \frac{kT}{h} \frac{Q_2^\ddagger}{Q_2} e^{(\epsilon_{0,2} - \epsilon_{0,2}^\ddagger)/kT}$$



Now, come to kinetic isotope effect; again, let us go for absolute reaction rate theory so you see there is a transition state then transition state to product it is also second transition state to product so for the first 1 this K 1 this is K 1 corresponding rate is a transmission then K T by H into K 1 double dagger it is it is given by this expression K 2 it is given by this expression. This is in terms of absolute rate constant K 1 and K 2 these are the corresponding partition functions this is the new part that is K T by H that is the mode which is responsible for the rupture of the bond. So, that is weak you know, vibrational mode which is converted to translation so that is this so anyway so K 1 and K 2 we have got the expression from you know, theory of reaction rates so K 1 and K 2. We have got the expression this is the this is your equilibrium constant for the formation of the absolute I mean activated complex that is your given by double dagger this is your activated complex.

(Refer Slide Time: 30:41)

$$\frac{k_1}{k_2} = \frac{\kappa_1 \sigma_1 \sigma_2}{\kappa_2 \sigma_2^\ddagger \sigma_1^\ddagger} \cdot \text{MMI} \cdot \text{EXC} \cdot \text{ZPE}$$

$$\text{EXC} = \frac{\sum_i^{3n-6} (1 - e^{-u_{i1}}) / (1 - e^{-u_{i2}})}{\sum_l^{3n-7} (1 - e^{-u_{l1}^\ddagger}) / (1 - e^{-u_{l2}^\ddagger})} \quad \text{ZPE} = \frac{\exp\left\{\sum_i^{3n-6} (u_{i1} - u_{i2}) / 2\right\}}{\exp\left\{\sum_l^{3n-7} (u_{l1}^\ddagger - u_{l2}^\ddagger) / 2\right\}}$$

*Approximations:*

$$\kappa_1 \cong \kappa_2, \quad m_2^\ddagger / m_1^\ddagger \cong m_2 / m_1, \quad I_2^\ddagger / I_1^\ddagger \cong I_2 / I_1; \quad \text{for}$$

$$v_1 > 500 \text{ cm}^{-1} \quad e^{-u_i} < 0.08 \text{ at } 25^\circ \text{C} \text{ and } \therefore \text{EXC} \cong 1.$$



Then it is your  $k_1$  by  $k_2$ ; you can write in terms of this that this mass moment inertia excitation term and 0 energy term. So, this term goes like this because,  $u_i$  is  $h \nu_i$  by  $kT$  and your 0 energy term goes like this of course, we have to use the appropriate you know, one to end of this double dagger term. This is your  $I$ ; for  $I$  for reactant side and  $I$  for your product side. Now, we have to make certain assumptions approximations that  $\kappa_1$  is equal to  $\kappa_2$  is very close transmission part is very close also  $M_2$  and  $M_1$  double dagger, these are you know, close to  $M_2$  by  $M_1$  that is the ratio of you know, basically this differing the mass which is differing  $I$  mean the hydrogen and deuterium and  $I_2$  double dagger and  $I_1$  double dagger may again be approximated to  $I_2$  by  $I_1$  for  $\nu_i$  greater than 500 centimetre inverse  $E$  to the power minus  $u_i$  is less than 0.8 at 25 degree centigrade and excitation term is of the order of and if this gives you excitation term of the order of unity.


(Refer Slide Time: 32:18)

$$\frac{k_1}{k_2} = \frac{\kappa_1 \sigma_1 \sigma_2}{\kappa_2 \sigma_2^\ddagger \sigma_1^\ddagger} \cdot \text{MMI} \cdot \text{EXC} \cdot \text{ZPE}$$

$$\text{EXC} = \frac{\sum_i^{3n-6} (1 - e^{-u_{i1}})/(1 - e^{-u_{i2}})}{\sum_l^{3n-7} (1 - e^{-u_{l1}^\ddagger})/(1 - e^{-u_{l2}^\ddagger})} \quad \text{ZPE} = \frac{\exp\left\{\sum_i^{3n-6} (u_{i1} - u_{i2})/2\right\}}{\exp\left\{\sum_l^{3n-7} (u_{l1}^\ddagger - u_{l2}^\ddagger)/2\right\}}$$

*Approximations:*

$\kappa_1 \cong \kappa_2$ ,  $m_2^\ddagger/m_1^\ddagger \cong m_2/m_1$ ,  $I_2^\ddagger/I_1^\ddagger \cong I_2/I_1$ ; for  $\nu_1 > 500 \text{ cm}^{-1}$   $e^{-u_i} < 0.08$  at  $25^\circ\text{C}$  and  $\therefore \text{EXC} \cong 1$ .



So, I mean, applying the absolute reaction rate theory we arrived that this expression then, we are making certain approximations and based on those approximations you know,  $k_1$  by  $k_2$  is this sigma factor. So, it is the symmetry number and then it is the 0 energy ZPE.


(Refer Slide Time: 32:25)

$$\frac{k_1}{k_2} = \frac{\sigma_1 \sigma_2^\ddagger}{\sigma_2 \sigma_1^\ddagger} \cdot \text{ZPE}$$

$$\epsilon_0 = \frac{h\nu}{2} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

*Rules:*

1. Isotopically heavier molecule has lower ZPE.
2.  $\Delta\text{ZPE}$  between isotopic isomers increases as  $f$  increases.
3. Heavier isotope accumulates in the state where binding is stronger (e.g. for C-L, where vibrational well is steeper).
4. Lighter isotope accumulates where binding is weaker.
5.  $\Delta\text{ZPE}$  is greatest for hydrogen isotopes.

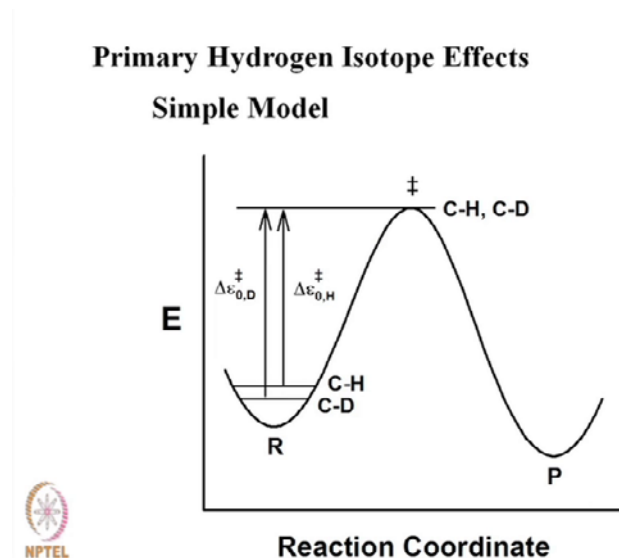


It depends on ZPE; so difference in ZPE - 0 energy -  $E_0$  is half  $h\nu$  and  $\nu$  is  $1$  by  $2\pi$  root over  $k$  by  $\mu$  or  $f$  by  $\mu$  and  $\mu$  is  $M_1 M_2$  by  $M_1 + M_2$ . We have arrived at the expression for your kinetic isotope effect that  $k_1$  by  $k_2$  is related to your 0 energy

So what we are getting? That isotopically heavier molecule has lower 0 energy as I already told u that for deuterium it is lower this one than 0 energy is lower compared to your C-H and delta ZPE between isotopic isomers increases as f increases. That is, frequency increases heavier isotopes accumulate in the state where binding is stronger and lighter isotopes accumulate where binding is weaker and delta Z P is greatest for hydrogen isotopes.

These are the rules that means isotopically heavier molecules has lower 0 energy delta ZPE between isotopic isomers increase as f increases heavier isotope accumulates in the state where binding is stronger lighter isotope accumulate; where binding is weaker and also delta ZPE the difference in 0 energy is greatest for hydrogen isotopes.

(Refer Slide Time: 34:34)



Simple model, that this is your reaction coordinate this is your reactant side this is your product side again using the similar model that this is your reactant surface I mean potential energy curve this product potential energy curve and we are moving from this side to that side; so reaction coordinate is in this direction. You see that this your transition state. So, to go to the transition state you have to put you have to put more energy put in more energy compared to this hydrogen and as I told you in the earliest slide that heavier isotopes accumulate in the state where binding is stronger. So, see heavier isotope is here than this one so that means it requires more activation compared to this lighter one. A lighter one means in order to reach the transition state that is the your C-H or C-D transition state for C-H it requires less for C-D; it requires more



because it is its 0 energy is less. That means, in order to activate this C-D I mean in order to have greater oscillation because there that bond has to be ruptured that means the oscillation. This oscillation has to be huge so that is why that bond will be that particular bond will be ruptured. This oscillation it is you know, large amplitude oscillation that will be converted to translation. But, for heavier one what is happening they are a little **(C)** compared to the lighter 1 so in order to activate them you need to put in more amount of energy. That means more of activation. More activation means this gap is more. As per Arrhenius theory, this rate will be slower compared to this rate.

(Refer Slide Time: 36:49)

All of reactant state  $\Delta ZPE_{H,D}$  is lost in the transition state:


$$\Delta ZPE_{H,D}^\ddagger = \Delta e_{0,H}^\ddagger - \Delta e_{0,D}^\ddagger$$

$$\frac{k_H}{k_D} = e^{-\Delta ZPE_{H,D}^\ddagger / kT}$$

$$\epsilon_0 = \frac{1}{2} hc \bar{\nu} \quad \Delta \epsilon_{0,H}^\ddagger = \epsilon_{0,H}^\ddagger - \epsilon_{0,H}^R$$

$$\Delta \epsilon_{0,D}^\ddagger = \epsilon_{0,D}^\ddagger - \epsilon_{0,D}^R$$

Since  $\epsilon_{0,H}^\ddagger = \epsilon_{0,D}^\ddagger$ :


$$\Delta ZPE_{H,D}^\ddagger = \epsilon_{0,D}^R - \epsilon_{0,H}^R = -\Delta ZPE_{H,D}^R$$


All of reactant state delta ZPE H D is lost in transition state. Therefore, delta ZPE H D is basically this one expression and  $k_H$  by  $k_D$  is basically  $E$  to the power minus delta ZPE double dagger divided by  $kT$  and  $E_0$  is half  $hC \bar{\nu}$  and  $\Delta E_{0,H}$  is this one and  $\Delta E_{0,D}$  is this one and also this one. They are they are located at the same. Therefore, delta ZPE is basically  $E_{0,D}$  and  $E_{0,H}$  from the reactant side so it is basically minus delta ZPE reactant side between H and D that is the 1 I just told you that this is the difference this is the difference that is this one because this particular 1 that is for C-H and C-D this transition state is identical.

(Refer Slide Time: 38:05)

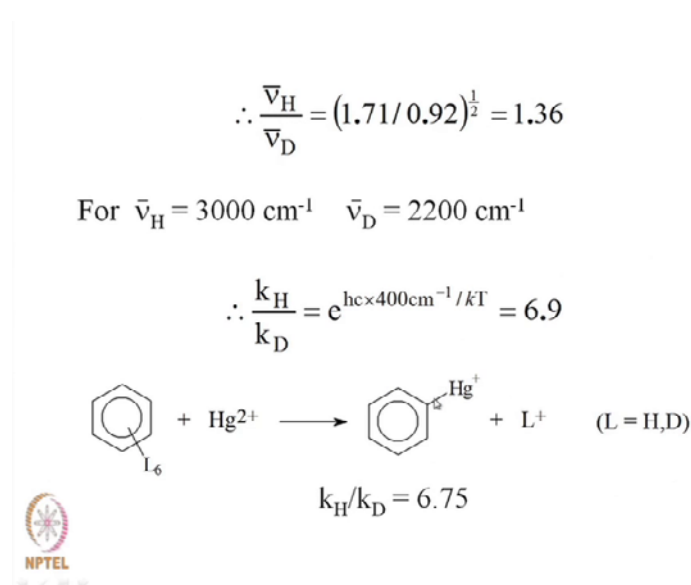
$$\therefore \frac{k_H}{k_D} = e^{(\epsilon_{0,H}^R - \epsilon_{0,D}^R)/kT} = e^{hc(\bar{\nu}_H - \bar{\nu}_D)/2kT}$$

$$\left. \begin{array}{l} \epsilon_{0,H}^R = \frac{1}{2}hc\bar{\nu}_H \quad \nu_H = \frac{1}{2\pi} \sqrt{\frac{f}{\mu_{C-H}}} \\ \epsilon_{0,D}^R = \frac{1}{2}hc\bar{\nu}_D \quad \nu_D = \frac{1}{2\pi} \sqrt{\frac{f}{\mu_{C-D}}} \end{array} \right\} \frac{\bar{\nu}_H}{\bar{\nu}_D} = \sqrt{\frac{\mu_{C-D}}{\mu_{C-H}}}$$

$$\mu_{C-H} = \frac{m_C m_H}{m_C + m_H} = 0.92 \text{ amu} \quad \mu_{C-D} = \frac{m_C m_D}{m_C + m_D} = 1.71 \text{ amu}$$


So,  $k_H$  by  $k_D$  is equal to this like this one and  $E_0$   $E_0$   $R_H$  is this  $E_0$   $R_D$  is this so  $\nu_H$  is this one  $f$  by  $\mu_{C-H}$  and  $f$  by  $\mu_{C-D}$  so since  $\mu_{C-D}$  is more than this one. Therefore, you see you see it it is calculated over here that  $\mu_{C-H}$  is 0.92 and  $\mu_{C-D}$  is 1.71;  $\mu_{C-D}$  is almost twice you see, 1.71 means it is 1.84 if you double it 0.92 and it is 1.71. So, almost double this  $\mu_{C-D}$  is almost double that of  $\mu_{C-H}$  you see. Therefore, your this  $\nu_D/\nu_H$  is you know,  $\sqrt{0.92/1.71}$  by  $\sqrt{1.71/0.92}$  it will have a factor of 1 by  $\sqrt{2}$ .

(Refer Slide Time: 39:20)



Therefore, what we are getting that it is  $1.36$  this square root of this is  $1.36$  so and for hydrogen it is  $3000$  centimetre inverse and for deuterium it is  $2200$  centimetre inverse

Again, if we go back to this slide that that this is the deciding factor this  $\mu$  is the real deciding factor and also this frequency this frequency I mean the it is related to the bond strength that is force constant so if we think that force constant is remaining same that this is the factor which is responsible for the difference in the rate of reaction so that is why that is why you know, isotope effect means looking into isotope effect is of great importance while discussing or while you know, while exploring some reaction mechanism. Therefore, if we take some concrete example that for you see for hydrogen  $\nu_{\text{H}}$  is  $3000$  centimetre inverse and deuterium it is  $2200$  centimetre inverse you know, it is it is a huge difference  $1.36$  times it is a huge difference  $1.36$  into  $\nu_{\text{D}}$  will give you  $3000$  you see that just  $1$  unit of increase of mass from hydrogen to deuterium has shifted the wave number corresponding to wave number corresponding to that particular vibration that is C-H or C-D vibration to enormously that is about  $800$  centimetre inverse. I mean, it is  $800$  centimetre inverse. So, you change your mass I mean, atoms mass by  $1$  unit and you will get about  $800$  centimetre inverse for hydrogen. Therefore,  $K_{\text{H}}$  by  $K_{\text{D}}$  you know,  $\frac{h\nu_{\text{H}}}{kT}$  divided by  $\frac{h\nu_{\text{D}}}{kT}$  if you do this then, you will be finding that how much you will be getting that it is  $6.9$  you see here divided by  $2$  that is why it is  $400$  showing to you  $400$  just plug in this expression  $\frac{K_{\text{H}}}{K_{\text{D}}}$  is equal to  $\frac{E_{0\text{H}}}{E_{0\text{D}}}$  reactant side  $\frac{E_{0\text{H}}}{E_{0\text{D}}}$  reactant side divided by  $\frac{K_{\text{H}}}{K_{\text{D}}}$  so it is the it is it is Boltzmann factor so  $\frac{E_{0\text{H}}}{E_{0\text{D}}}$  into  $\frac{\nu_{\text{H}}}{\nu_{\text{D}}}$  divided by  $2$   $\frac{K_{\text{H}}}{K_{\text{D}}}$  because this because of this one half  $\frac{h\nu_{\text{H}}}{kT}$  because this raise is half  $\frac{h\nu_{\text{H}}}{kT}$  and you can get this number from means, you can if you consult any standard quantum chemistry textbook under harmonic oscillator. So, it is an exactly solvable model so if you if you consult any standard quantum mechanics or quantum chemistry text then you will be getting you will be finding that it is half  $\frac{h\nu_{\text{H}}}{kT}$  it is the  $0$  energy. That is even if you go to absolute  $0$  temperature the residual vibration will be this much this will remain, be there means, it will never stop vibrating; even if you go to absolute  $0$  temperature. If it stops vibrating then it will violate your uncertain relation. Therefore, your  $\frac{K_{\text{H}}}{K_{\text{D}}}$  is this so it is  $6.9$  and if you take some concrete example that benzene with  $1.6$  were  $1$  is H or D and if you consider this reaction with  $\text{H}_2$  plus then you can get  $\frac{K_{\text{H}}}{K_{\text{D}}}$  is equal to  $6.75$ , almost close to  $7$ . So, that means it is a huge amount of you know, isotope effect and since these you know, in this case the reaction I mean this

H g plus is replacing this hydrogen. So, directly it is replacing this hydrogen or deuterium. In that case, that is why you are getting a high amount of high amount of effect.


(Refer Slide Time: 44:49)

**Deuterium Isotope Effect  
(Kinetic Isotope Effect)**

- Important in elucidation of reaction mechanisms
- Cleavage of C-H and C-D requires different amount of energy

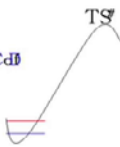
Hooke's Law, Stretching frequencies, IR


$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f(m_1+m_2)}{m_1 m_2}}$$



$\tilde{\nu}$  C-H: ca 3000  $\text{cm}^{-1}$   
 $\tilde{\nu}$  C-D: ca 2200  $\text{cm}^{-1}$

$E^0 = 1/2h\nu$   
 $E^0$  C-H 18 kJ/mol  
 $E^0$  C-D 13 kJ/mol  
 Higher activation energy for cleavage of C-D  
 Cleavage of C-H will be faster





So, what we have? Why do we need to you know, study deuterium isotope effect specially the primary kinetic isotope effect? Now, this is very important because, for the elucidation of your mechanism whether your rate determining step is you know, involving any hydrogen abstraction or hydrogen addition. Or, it directly involves any hydrogen atom or not that we can predict so that means you take a deuterated substance in 1 case and in another case, you take a non-deuterated I mean hydrogenated substance and find out you know, study the kinetics of the reaction at a given say temperature so you keep the temperature fixed. Otherwise, you would not be able to you would not be able to you know, get the idea whether if any difference is at all there is due to difference in temperature or not. So, that means at a fixed temperature, you study the kinetics in presence of a deuterated substance and in second case in presence of a hydrogenated substance so it will give you the idea it will give you the indication that whether that particular hydrogen which is. Now, replaced with deuterium is involved in a in a specific you know, step of the reaction that is you can you can judge the mechanism of the reaction also since the cleavage of hydrogen C-H bond and cleavage of deuterium C-D bond requires different amount of energy that is the you know, catchy. That is the catchy.

That we want to exploit that information that is whether that is doing something that difference is doing something on the kinetics of the process.

So, if we go back to the earlier slide that you know, you see that after doing this calculations you know, using absolute reaction rate theory if you do this numbers you know, I mean these expressions and you see that ultimately with certain approximations we get these 1 that it indeed depends on this  $K_1/K_2$  this ratio indeed depends on the  $E_0$  energy that is the difference in  $E_0$  energy of the concerned bond it is very important and isotopic ally heavier molecule naturally will have lower  $E_0$  energy and also the heavier isotopes accumulate in the state where binding is strong they will tend to tend to accumulate to the to the lower portion then the then the you know, heavier I mean lighter 1 so and the lighter 1 will accumulate towards the upper portion so that is why that is why it is it is very interesting and it is very informative. Now, Hooke's law stretching frequencies is that  $\bar{\nu}$  is equal to  $1/2\pi C \sqrt{K/\mu}$  so that means if you have a if you have a heavier mass then its it will oscillate slow if you replace with a  $(C)$  it will oscillate fast.

That gives the difference that gives a difference means faster oscillation means faster probability of rupture of this bond I mean I mean more probability of rupture of this bond. If it oscillates slowly that means it takes time kinetically it is a slower one. So, if it is doing very fast if it is doing very fast then, that means it is it has got the more probability to get ruptured the bond has the more probability to get detached. I mean, the rupture of the bond but, if it is doing slowly then of course, it will do but, extent is less and that gives you the idea I mean I mean it is very clear from your frequency number I mean wave number it is 3000 for C-H and 2200 for your deuterium and  $E_0$  is half H nu it is from you can you can get it from quantum mechanics  $E_0$  for C-H is more than  $E_0$  for C-D and higher activation energy for C-D. Then, for hydrogen cleavage of C-H as I told you will be faster.

So, it is really you know, very informative and interesting and you see that your this is this redline this is for hydrogen blue line is for deuterium and this is your reaction side this is your transition state side so that means to reach the transition state this one will require less energy this one will require more energy. Therefore, we must say 1. That deuterium isotope effect that is you know, primary kinetic isotope effect is indeed very useful in studying or in elucidating the K reaction mechanism specially the organic

reactions where there is a lot of you know, hydrogen rearrangement I mean proton rearrangement or maybe hydrogen atom rearrangement whether in the rate determining step this hydrogen is rearranged or not.

That will give us the enormous information on the on the on the proposed you know, or plausible mechanism that is we propose a plausible mechanism and then we try to match with the experiment other experimental results. In that case, we can punch this information that that is the deuterium isotope effect whether this isotope effect is there or not, so that will help to elucidate you know, the mechanism. It is basically your primary kinetic isotope effect, there is another kinetic isotope effect which is called the secondary kinetic isotope effect that in that case you know, if you replace you know, a hydrogen which is at a distant place from the reaction centre and even if you get  $k_H$  by  $k_D$  which is not exactly directly related your reactions centre. That is called your secondary kinetic isotope effect and in that case  $k_H$  by  $k_D$  is not it will not come to be very close to 7; it will be less maybe less than 4.

So, with this we conclude the isotope effect. So, in our next piece of lecture we will talk on; we will continue to talk and we will talk on this fast kinetics. That is the reactions which are which are very fast; maybe diffusion control or maybe even you know, it is may be in the ultra fast time scale maybe in picoseconds time scale; maybe in fem to second time scale; maybe some photo physical processes; maybe some photo chemical processes. So, we will take up all those issues from our next classes till then have a nice time; thank you.