

## 7. How Do You Know Which Way Reactions Go?

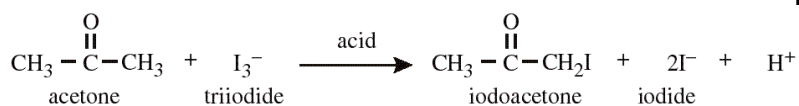


March 10, 2000

The exam 1 date and time :

Monday, March 20, 4:30-6:00 PM in [CB321](#)

## The Halogenation of Acetone



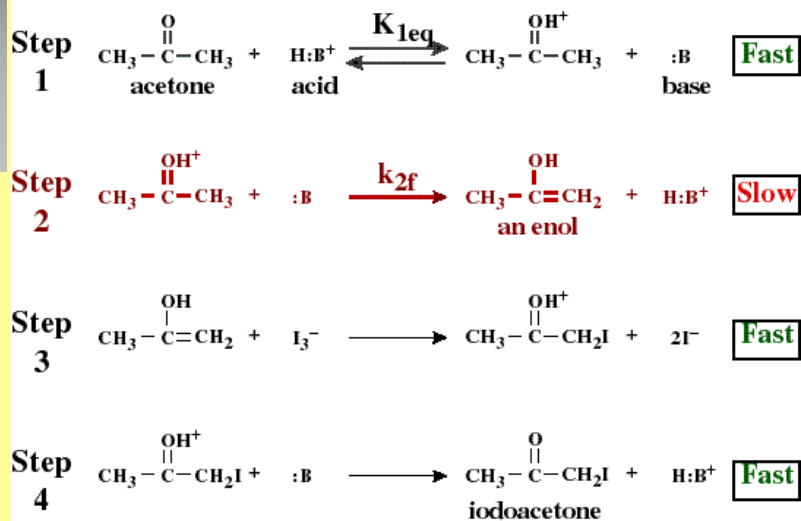
(all reactants and products aqueous)

rate **is not** =  $k[\text{CH}_3\text{COCH}_3][\text{I}_3^-]$   
thus the above reaction **is not** the mechanism of the  
reaction.

The observed rate law is:

$$\text{rate} = -\frac{d[\text{I}_3^-]}{d(\text{time})} = k[\text{H}^+][\text{CH}_3\text{COCH}_3]$$

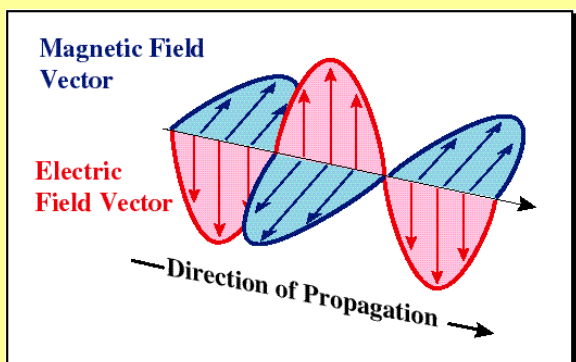
## The Mechanism of the Halogenation of Acetone



## Determining the Reaction Order

- **Strategy-** under conditions of flooding, hold all concentrations but one constant.
- **Example:** For rate =  $[\text{H}^+]^x [\text{CH}_3\text{COCH}_3]^y$ 
  - run A- 1 mL of 0.33-M HCL & 2 mL acetone with a total reaction volume of 6 mL.
  - run B- 2 mL of 0.33-M HCL & 2 mL acetone with a total reaction volume of 6 mL.
- Since the concentration of  $[\text{H}^+]$  double from run A to B the rate is expected to :
  - stay the same if  $x=0$
  - double if  $x=1$
  - quadruple if  $x=2$ .

## Light Waves (electromagnetic radiation)



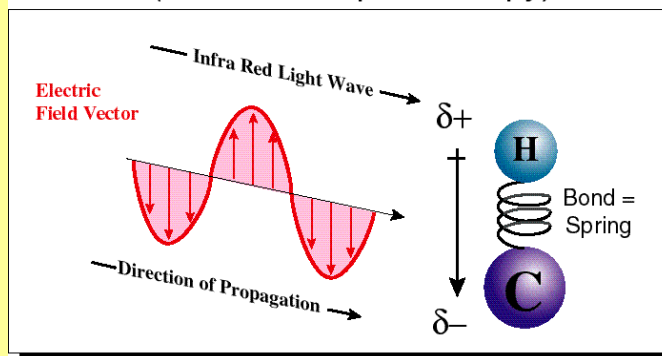
$$E = h \nu$$

$$\nu = \frac{c}{\lambda}$$

**E=Energy(J), h=Plank's constant (J•s),  
ν=frequency(s<sup>-1</sup>), c= speed of light(m/s),  
and λ=wavelength(m).**

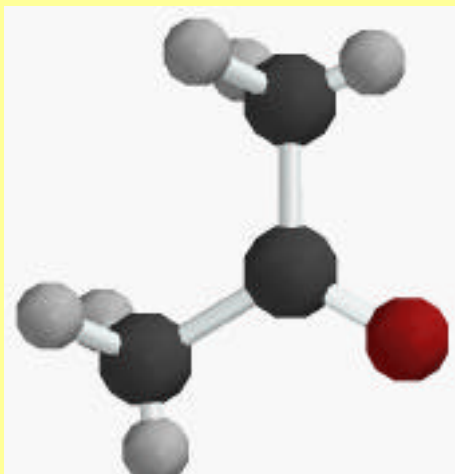
## IR Spectroscopy (vibrational spectroscopy)

### Infrared Spectroscopy (Vibrational Spectroscopy)



When the frequency of the light matches (is resonant with) the frequency of the vibration, light is strongly absorbed.

## One Acetone Vibration

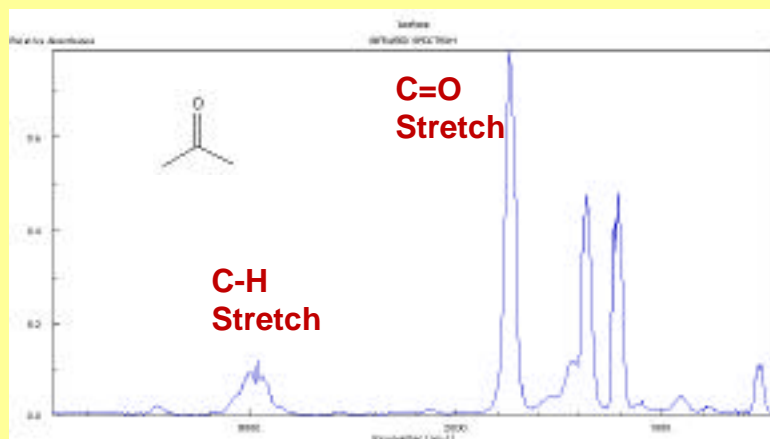


Recall for H<sub>2</sub>O there were Three types of Vibrations.

- Symmetric
- Asymmetric
- Scissors

(each with it's own frequency)

## IR Spectrum of Acetone

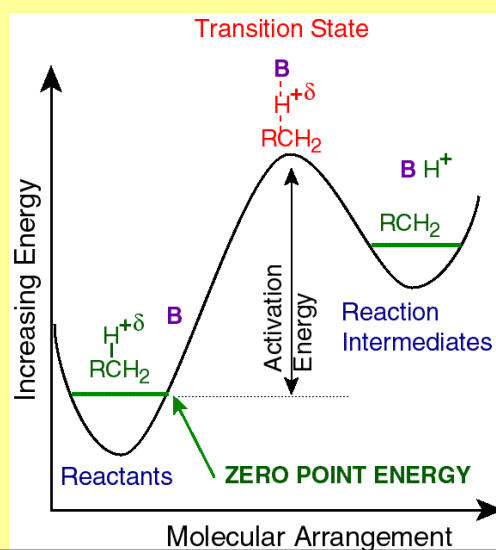


From: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C67641&Units=SI&Mask=80>

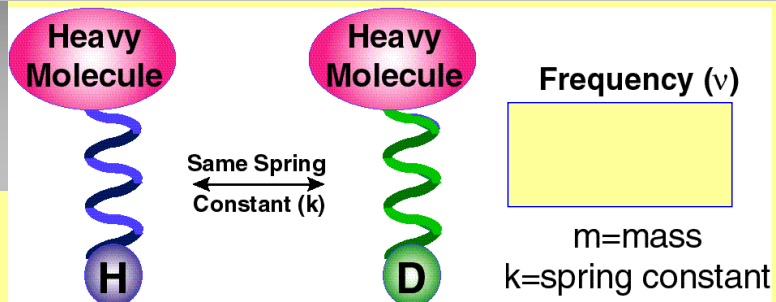
## *Kinetic Isotope Effect*

- Atoms in molecules vibrate at discrete frequencies. Quantum mechanics can be used to show why the energies are quantized.
- The lowest vibrational energy is  $E_0 = \frac{1}{2} (h \nu_{\text{vib}})$ , called the zero point energy. (Recall, in the particle in the box the energy can not be 0.)
- The vibrational frequency can be probed using infra red spectroscopy.
- A protons (bonded to carbon) typically vibrate at about  $\nu_{\text{vib}} = 9 \times 10^{13} \text{ s}^{-1}$  (by infra red spectroscopy, i.e.  $3000 \text{ cm}^{-1}$ ).

## *Reaction Coordinate*

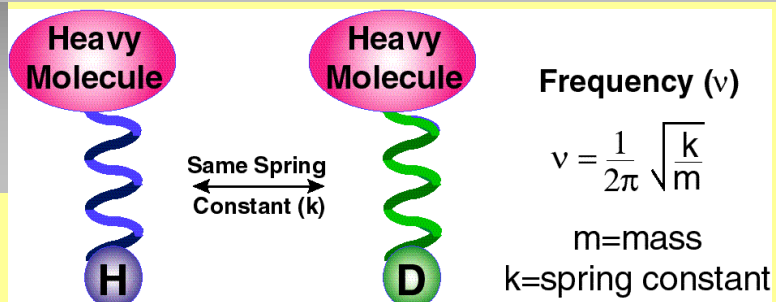


## Vibrational Frequency



Experiment	Can 1band	Can 2 band	Half full 1 band
Cycles in 30s			

## Vibration of $^1\text{H}$ and $^2\text{D}$



- A proton ( $^1\text{H}$ ) has half the mass of a deuteron ( $^2\text{D}$ ) and is expected to vibrate  $\sqrt{2}$  faster than a deuteron.
- From IR,  $^2\text{D}$  bonded to carbon vibrates at about  $9 \times 10^{13} \text{ S}^{-1} / \sqrt{2} = 6.4 \times 10^{13} \text{ S}^{-1}$ .

## *Activation Energy-Arrhenius Law*

### ■ Arrhenius Law

$$k = \text{reaction constant} = Ae^{-E_a/RT}$$

where R is the gas constant {8.31 J/(K•mol)}, A is the collision factor,  $E_a$  is the activation energy, and T is the temperature (in Kelvin!).

### Alternate form:

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

## *Interpretation of Arrhenius Law*

- The factor A, can be interpreted as the frequency with which molecules are found in the proper configuration to react.
  - For example, in a simple bimolecular reaction, the factor A would represent the frequency of collisions between molecules with the correct configuration to react?
- The factor  $e^{-E_a/RT}$  is interpreted as the fraction of molecules that have enough energy to react.

## Vibrational Energies

- The energy is obtained from the vibrational frequency by the relation-

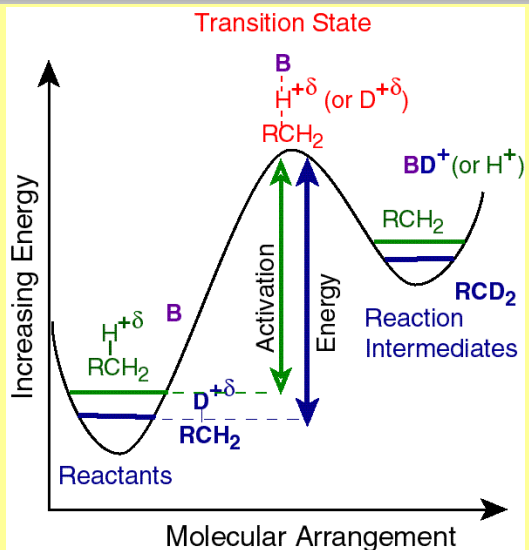
$$\text{Energy} = N_A h \nu$$

- $N_A$  is Avagadro's number  $6.02 \times 10^{23}/\text{mol}$
- $h$  is Planck's Constant  $= 6.626 \times 10^{-34} \text{J}\cdot\text{s}$
- $\nu$  is frequency (in 1/Sec)

- The difference in zero points energies between  $^1\text{H}$  and  $^2\text{D}$  is therefore

- $E = \frac{1}{2} N_A h (\nu_{\text{hydrogen}} - \nu_{\text{deuterium}}) = 5260 \text{ J/mol}$

## $^1\text{H}$ vs $^2\text{D}$ Reaction Diagram



## The Reaction Mechanism?

A **Reaction mechanism** is the sequence of bond-making and bond-breaking that occur during the conversion of reactants to products.

- The **order of a reactant** in a rate law can be taken to be the coefficient of the balanced reaction **if the reaction is an elementary mechanistic step in the reaction.**
- Theoretical reaction mechanisms can be compared to experimental rate law to test the validity of the models.

## *Qualitative Picture of the Kinetic Isotope Effect*

- The energy (vibrational frequency) of  $^1\text{H}$  and  $^2\text{D}$  are the starting energies (zero point energies). Therefore the potential of  $^2\text{D}$  is deeper than the potential of  $^1\text{H}$ .
- The vibrational frequency of  $^1\text{H}$  and  $^2\text{D}$  is about the same in the transition state (the spring constant is about zero, i.e. a very floppy bond).

## Quantitative Picture of the Kinetic Isotope Effect

- The rate that a molecule reacts is proportional to the factor  $e^{-E_a/RT}$ , and the difference in the activation energy is ~5 KJ/mol.
- This predicts

$$\frac{k_H}{k_D} = e^{-\frac{5260\text{J/mol}}{8.31\frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot 298\text{K}}} = e^{2.1} \approx 8$$

a ratio of ~7-8 for  $k_H/k_D$  is expected in reactions in which a proton-carbon bond is the rate limiting step. **BIG EFFECT!**

## Summary

- You will measure the rate of acetone iodination using optical spectroscopy.
- You will verify that the rate law is:  
$$\text{rate} = -\frac{d[\text{I}_3^-]}{d(\text{time})} = k[\text{H}^+][\text{CH}_3\text{COCH}_3]$$

and that the rate law is consistent with the mechanism given in the laboratory manual.
- You will verify that when deuterium labeled acetone used, the rate is decrease by a factor of approximately seven. This is strong evidence for C-H bond breaking in the rate determining step (the slow step)!