



## LECTURE 6

METO/CHEM 637  
**ATMOSPHERIC CHEMISTRY**  
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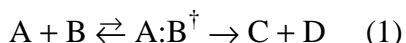
### OUTLINE

#### III KINETICS

F. Transition State Theory  
G. Experimental Techniques  
Finlayson-Pitts Ch. 4

#### TRANSITION STATE THEORY

The collision theory tells how frequently hard spheres the size of molecules bump into each other, and allows the calculation of the efficiency of a reaction, that is provides the maximum possible rate. Unfortunately, collision theory tells us nothing about steric factors or the activation energy, and these parameters must be determined experimentally. To calculate rate constants, we need to consider the chemical properties of the reactants and the activated complex for the steric factors. This is done with either a statistical mechanical or chemical thermodynamic approach in "Transition State Theory."



REACTANTS  $\rightleftharpoons$  ACTIVATED COMPLEX  $\rightarrow$  PRODUCTS

If the activated complex and reactants are in equilibrium then the equilibrium constant for this first step is:

$$K^\ddagger = \frac{k_f}{k_r} = \frac{[A:B^\ddagger]}{[A][B]} = \frac{Q_{AB^\ddagger}}{Q_A Q_B} \exp\left[\frac{-\Delta E_0}{RT}\right]$$

Where  $\Delta E_0$  is the difference in energy between the lowest energy level of the transition state and the reactants. Q's are partition functions, related to the probability that a molecule will be in a given energy state.

$$Q_{\text{total}} = Q_{\text{trans}} \times Q_{\text{rot}} \times Q_{\text{vib}} \times Q_{\text{elect}}$$

$$Q_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

$$Q_{\text{rot}} = \frac{(8\pi^2IkT)}{\sigma h^2}$$

$$Q_{\text{vib}} = \frac{kT}{h\nu_{\text{vib}}}$$

Where  $V$  is the volume,  $\sigma$  is a symmetry term,  $\nu_{\text{vib}}$  is the vibrational frequency, and  $I$  is the moment of inertia.

The partition functions,  $Q$ 's, come from the Boltzmann distribution, and give the distribution of translational, rotational, vibrational and electronic energy states. For the reactants, one can use conventional techniques such as those described in Moore's *Physical Chemistry*, Chapt. 9 to calculate  $Q$ . For the activated complex, it is harder.

The frequency of break up of the transition state (the last step in reaction 1 above) is often represented as  $\nu$ . This rate coefficient,  $\nu$ , can be thought of as a vibrational mode in the transition state becoming a translational mode. It can be estimated as the vibration frequency of a diatomic molecule undergoing vibrational excitation. From the above argument:

$$d[C]/dt = k_1[A][B] = \nu_{\text{vib}}[A:B^\ddagger]$$

Transition states ( $A:B^\ddagger$ ) usually have loose bonds with respect to vibrations.

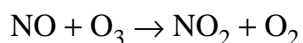
$$\frac{[A:B^\ddagger]}{[A][B]} = kT/h\nu_{\text{vib}} \frac{Q^\ddagger}{Q_A Q_B} \exp(-E_0/RT)$$

Notice that the preexponential factor is proportional to  $T$  and not  $T^{1/2}$  as in collision theory. A large activation energy, however, will still dominate the temperature dependence. We can separate out the rate coefficient:

$$k_f = kT/h \frac{Q^\ddagger}{Q_A Q_B} \exp(-E_0/RT)$$

Here, the  $k$  is the Boltzmann  $k$ ; note that  $kT/h$  is  $6.25 \times 10^{12} \text{ s}^{-1}$  at 300 K, but  $Q^\ddagger$  and  $E_0$  must be determined experimentally. This expression from transition state theory (or activated complex theory) is generally more useful than hard sphere collision theory. Although the partition functions are difficult to calculate, at least they depend on the molecular properties.

We can approximate  $Q^\ddagger$ . Each translational degree of freedom is worth roughly  $10^8 \text{ cm}^{-1}$ ; each vibrational degree of freedom is worth roughly  $10 \text{ cm}^{-1}$  and each rotational degree of freedom is worth roughly 1. Note that one vibrational degree of freedom in the transition state is lost to the dissociation. Thus for



$$A = kT/h \frac{Q^\ddagger}{Q_A Q_B} \approx kT/h \frac{q_t^3 q_r^3 q_v^8}{(q_t^3 q_r^2 q_v^1)(q_t^3 q_r^3 q_v^3)} = \frac{q_v^4}{q_t^3 q_r^2} = 6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$$

We can also approach the rate of the reaction from a chemical thermodynamics point of view. Remembering the definition of Gibb's free energy:

$$K_{\text{eq}} = \exp(-\Delta G^\ddagger/RT) = \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R)$$

Where  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the Gibbs free energy, enthalpy and entropy changes in going from the reactants to the transition state.  $\Delta H^\ddagger$  is really the same as the activation energy. Remembering that the rate of product formation can be related to the vibrational frequency of the transition state:

$$\begin{aligned} d[C]/dt &= \nu_{\text{vib}}[A:B^\ddagger] = \nu_{\text{vib}} K_{\text{eq}} [A][B] \\ &= \nu_{\text{vib}} \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R) [A][B] \end{aligned}$$

The rate coefficient is now:

$$k_f = \frac{kT}{h} \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)$$

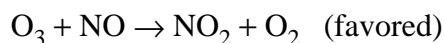
The preexponential factor now contains a temperature independent factor for the entropy of the transition state. This considers the steric effects talked about in collision theory. The more highly ordered the transition state, the more negative the entropy, and the smaller the preexponential factor and the slower the reaction.

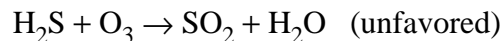
#### General Rules for Transition States

1. The more degrees of freedom in  $A:B^\ddagger$  the **smaller** the preexponential factor. (Degenerate degrees of freedom do not count.)
2. A more ordered activated complex means a smaller preexponential factor for the rate constant.
3. Multiple bond breaking and forming is unfavored.

By drawing possible configurations for the transition states, one can estimate the  $\Delta S^\ddagger$  and the rate coefficient of a reaction. See for example Jeong and Kaufman, *J. Phys. Chem.* (1982) and Gaffney and Levine (1979).

#### EXAMPLES





NOTE: Gibbs free energy for the last reaction is highly favorable.

$$\Delta G = -157.6 \text{ kcal/mole}$$

But the entropy factor is highly unfavorable. You can't draw a simple transition state, and many bonds have to be broken and reformed. The measured rate coefficient is:

$$k = 7 \times 10^{-14} \exp(-3400/T)$$

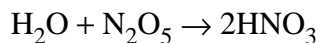
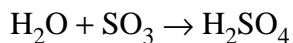
At 298 K

$$= 8 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$$

At atmospheric pressure, if the  $[\text{O}_3]$  is 30 ppb and constant, the lifetime of  $\text{H}_2\text{S}$  is quite long with respect to this reaction.

$$\begin{aligned} \tau &= (k[\text{O}_3])^{-1} = (8 \times 10^{-19} \times 30 \times 10^{-9} \times 2.5 \times 10^{19})^{-1} \\ &= 1.7 \times 10^6 \text{ s} \approx 20 \text{ days} \end{aligned}$$

Projects for students: The rate constant for the reaction of  $\text{H}_2\text{S}$  with  $\text{OH}$  is  $5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and the mean  $\text{OH}$  number density is  $5 \times 10^5 \text{ cm}^{-3}$ . How do these two loss mechanisms compare? Try to draw transition states (activated complexes) for the following reactions. Calculate the Gibbs free energy of the reaction, and estimate the rate constant at room temperature. Experimentally determined rate coefficients are available for comparison.

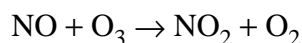




For bimolecular reactions we can approximate the partition function quotients.

{VIEWGRAPH}

As an example we calculate the rate constant for a diatomic and a nonlinear triatomic molecule.



The steric factor calculated from the partition coefficients is  $10^{-4}$ , thus:

$$A = A_{\text{max}} \times 10^{-4}$$

$$k_f = 3.0 \times 10^{-10} \times 10^{-4} (T/300)^{1/2}$$

Note, however that the temperature dependence could have been  $-3/2$ .

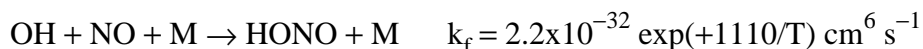
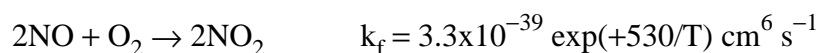
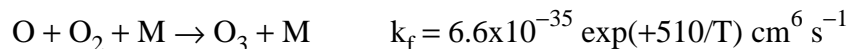
$$k_{300} = 3.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \text{ vs. } 1.6 \times 10^{-14} \text{ measured}$$

$$k_{400} = 5.3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \text{ vs. } 5.6 \times 10^{-14} \text{ measured}$$

### Termolecular Reactions

Third order (termolecular) reactions often proceed slower at higher temperatures and thus have negative activation energy.

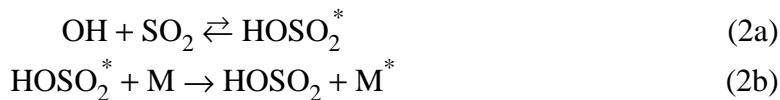
#### Examples



We can think of the negative activation energy as a result of the energy released by the formation of the activated complex making the transition state unstable unless a collision removes that excess energy. Another way of looking at this is to consider the process as proceeding in several steps. (Finlayson-Pitts, Section 4-A-4). Let's look at the first step in the formation of sulfuric acid from  $\text{SO}_2$ .



The net reaction can be considered as the sum of Reactions 2a and 2b where 2a is reversible and 2b is not.



$$-d[\text{SO}_2]/dt = k_2[\text{SO}_2][\text{OH}][\text{M}]$$

$$-d[\text{SO}_2]/dt = k_{2b}[\text{HOSO}_2^*][\text{M}]$$

$$k_2[\text{M}] = \frac{k_{2b}[\text{HOSO}_2^*][\text{M}]}{[\text{SO}_2][\text{OH}]}$$

If the concentration of the activated complex is not changing with time, i.e. it is in steady state then:

$$k_2[\text{SO}_2][\text{OH}][\text{M}] = k_{2b}[\text{HOSO}_2^*][\text{M}]$$

$$\frac{d[\text{HOSO}_2^*]}{dt} = 0 = k_{2a}[\text{SO}_2][\text{OH}] - k_{-2a}[\text{HOSO}_2^*] - k_{2b}[\text{HOSO}_2^*][\text{M}]$$

$$[\text{HOSO}_2^*] = \frac{k_{2a}[\text{OH}][\text{SO}_2]}{k_{-2a} + k_{2b}[\text{M}]}$$

Rewriting  $k_2\text{M}$ , the effective bimolecular rate constant, and substituting for  $[\text{HOSO}_2^*]$ ,

$$k_2\text{M} = \frac{k_{2b}k_{2a}[\text{M}]}{k_{-2a} + k_{2b}[\text{M}]}$$

At low pressure  $k_{-2a} \gg k_{2b}[\text{M}]$ , thus:

$$k_2 \approx \frac{k_{2b}k_{2a}}{k_{-2a}}$$

If each of these reactions has an activation energy, we can add them up:

$$k_2 = A_2 e^{(-E_a/RT)} = \left( \frac{A_{2a}A_{2b}}{A_{-2a}} \right) e^{(-(E_{2a} + E_{2b} - E_{-2a})/RT)}$$

If the activation energy for the reverse of Reaction 2a is larger than the sum of activation energies for reactions Reactions 2a and 2b, then the net activation energy will be negative. The measured rate constant (Atkinson et al., 1989) is

$$k_2 = 5.0 \times 10^{-31} (T/300)^{-3.3} \text{ cm}^6 \text{ s}^{-1}$$

with a high pressure limit of

$$k_{2\infty} = 2.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

This corresponds to an activation energy of about -1 kcal/mole.

### III.G Experimental Techniques See: Finlayson-Pitts, Chapter 4

Reactions of atmospheric interest often involve unstable or short-lived species, thus special techniques are required to measure their concentrations and to determine the rate constants.



### III.G Experimental Techniques

- Try to maintain pseudo-first order conditions.
- Observe the disappearance of one of the reactants.
- Maintain steady state conditions if possible.

Example: **Fast Flow Systems (FFS)**



**d** is the distance from the mixing point.

**v** is the linear velocity (ca. 10 m/s).

**t** is the reaction time or **d/v**.

- **Plug flow** conditions

P = 0.5 to 10 torr

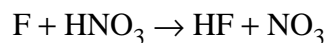
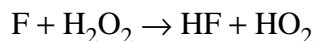
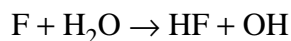
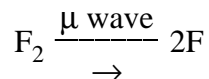
P too high, radial diffusion too slow

P too low, axial diffusion too fast

## Fast Flow Discharge System (FFDS)

### VIEWGRAPH

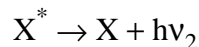
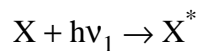
Short-lived reactants are generated in a microwave discharge. Such an electrodeless discharge system can dissociate diatomic molecules such as  $O_2$ ,  $N_2$ ,  $F_2$ , or  $Cl_2$  to produce O, N, F, or Cl atoms. Generating species such as HOx radicals poses a special problem, and they are often made in a two-step process.



### Detection Techniques

1. **Optical Absorption** - Simple Beer's law absorption can be applied, but only to species with a large absorption cross section. The short pathlength of the FFDS cell limits change in light intensity and thus the sensitivity.

2. **Fluorescence** - The gas of interest is illuminated with a collimated light beam, exciting the target species electronically, the excited atoms or molecules then reemit radiation in all directions. The detector is set at some angle relative to the excitation source to avoid measuring that incident light. The process can be represented by the following equations:



where

$$v_1 \geq v_2$$

High energy radiation, usually in the visible or uv, is required to initiate the electronic transition. This technique is especially useful for atoms and simple molecules and radicals that have discrete narrow absorption lines such as H, O, Cl, OH, but can be used to detect some more complicated species including  $H_3CO$ ,  $C_2H_5O$ , and  $NO_3$ .

The light source is usually a microwave discharge lamp, filled with the species of interest in a bath of inert gas such as He. The mixture flows through a microwave cavity where a

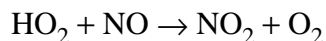
plasma is initiated with a Tesla coil. This lamp then produces radiation of exactly the correct wavelength, and the process is *resonance* fluorescence. Such lamps are cheap and reliable.

#### VIEWGRAPH

Fluorescence works even better if a laser can be found at the correct wavelength. **Laser Induced Fluorescence** (LIF) is especially sensitive because the intensity is very high and the excitation beam is coherent. LIF can detect OH radicals at molecular number densities as low as  $10^6 \text{ cm}^{-3}$ .

3. **Electron Spin Resonance** - Paramagnetic species (those with an unpaired electron) can be detected through the change in energy involved in the reversal of the spin of the electron. The energy levels associated with different spin orientations are split by a magnetic field in what is called the Zeeman effect. The splitting is proportional to the strength of the applied field. The species of interest is housed in a microwave cavity and the magnetic field is varied until the energy of the transition corresponds to the energy of the microwaves, i.e. is in resonance. The technique provides the absolute concentration and is nondestructive, but is limited in sensitivity, and only works for paramagnetic atoms and molecules.

4. **Laser Magnetic Resonance** - Similar in principle to ESR, a far IR ( $\geq 30 \text{ cm}^{-1}$ ) laser is used to induce a transition in an atom or molecule, while a magnetic field is swept to bring the energy of the line into resonance with the energy laser. LMR provides high specificity and sensitivity for species such as HO<sub>2</sub> radicals which are detected at levels as low as  $10^8 \text{ cm}^{-3}$ . Howard and Evenson (*Geophys. Res. Lett.*, 1977) remeasured the rate of



and knocked atmospheric chemistry into a cocked hat.

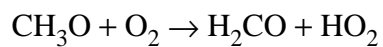
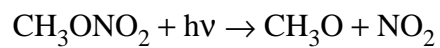
#### VIEWGRAPH

#### Flash Photolysis

#### VIEWGRAPH

Some very short-lived species can best be produced by photolysis. In flash photolysis (FP) a high-intensity lamp, such as a Xe lamp, is discharged for a split second into a reaction chamber. The UV radiation dissociates the molecules into unstable species that then react quickly. The rate of loss of the reactants is monitored with a technique such as resonance fluorescence. Because the products of the reaction tend to gunk up the reactor, a flow system is generally used. This also allows the results from numerous flashes to be averaged. A wide range of pressures can be employed.

Gutman et al. (*J. Chem. Phys.*, 1982) used alkyl nitrates and PF-LIF to study the kinetics of methoxy and ethoxy radicals:



The only Nobel Prize ever awarded in kinetics went to R. G. W. Norrish (Cambridge) for developing the technique of flash photolysis. See for example Norrish and Porter (*Nature*, 1950).