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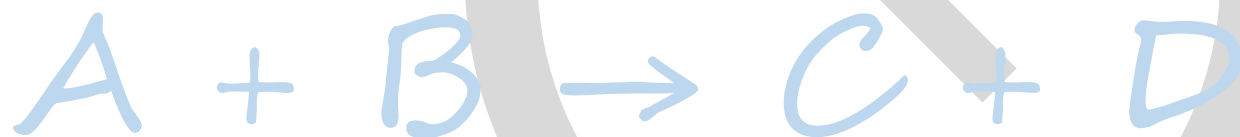
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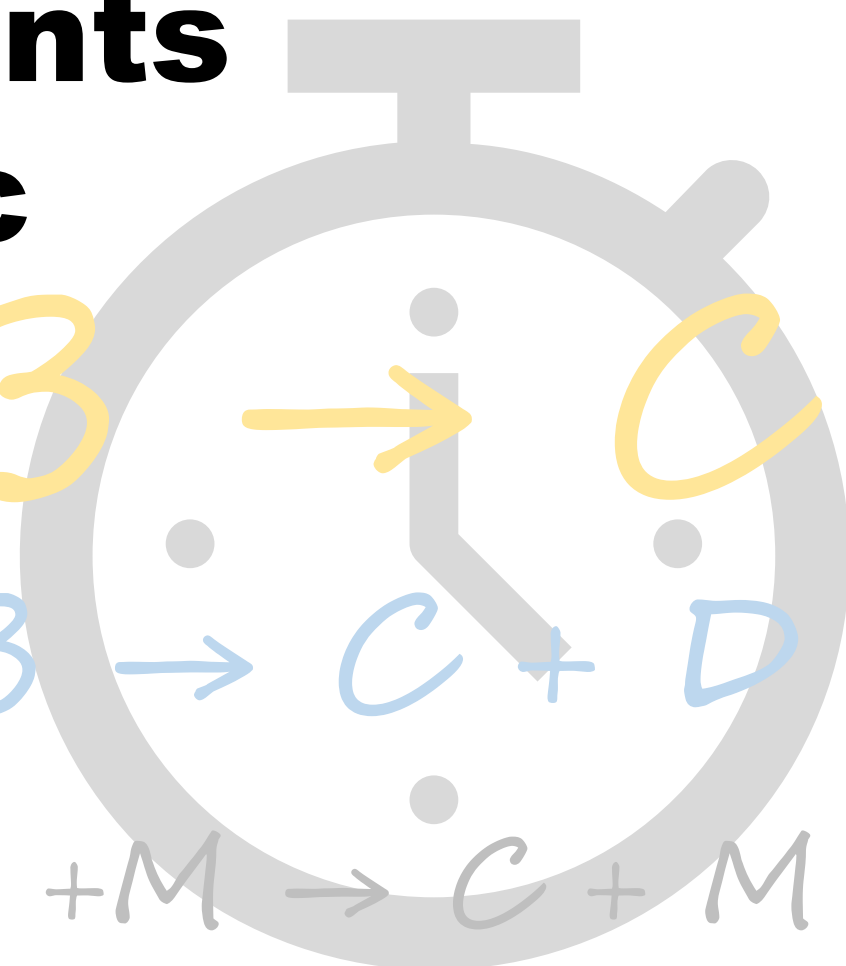


Laboratory experiments for measuring kinetic parameters



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France



Lecture outline

- Why should we care about chemical kinetics?
- Lifetime in the atmosphere
- The nature of the rate coefficient, k
 - What is it?
 - The gas-kinetic limit
 - The Arrhenius equation
- Methods for measuring k
- Dependence of k on T and P
- The problem with parameter-space

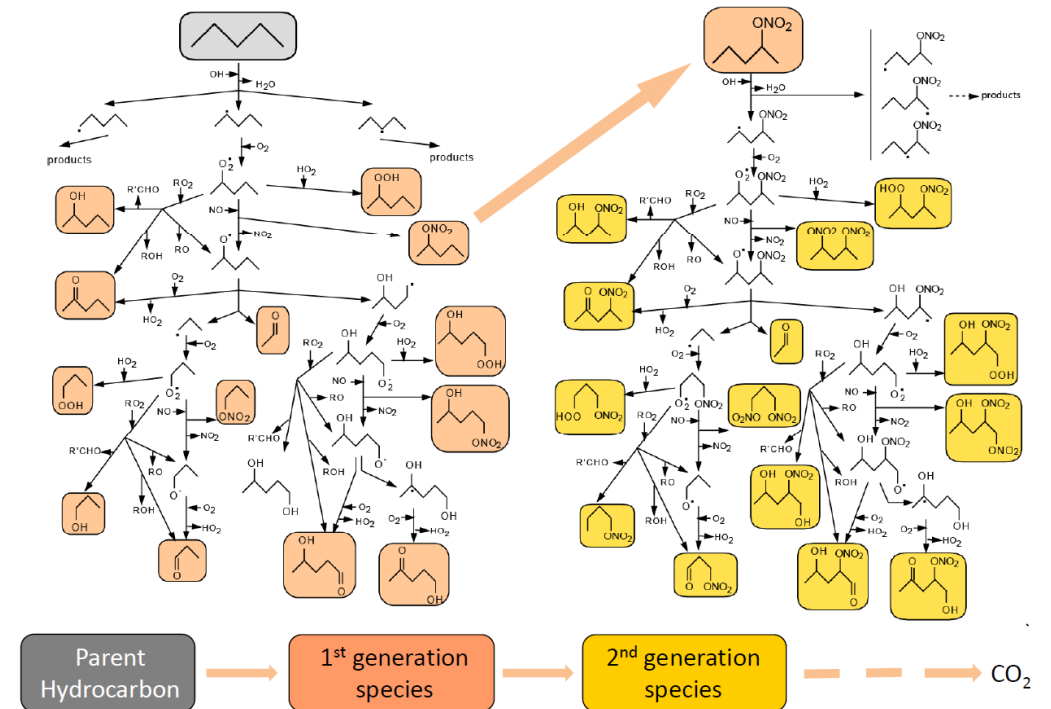
Kinetic parameters of the atmosphere

Carte du jour

- Photolysis:
 - $O_3 + hv \rightarrow O(^1D) + O_2$
- Thermal decomposition:
 - $CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO + NO_2$
- Radical–molecule:
 - $OH + \text{isoprene} \rightarrow \text{products}$
- Radical–radical:
 - $RO_2 + RO_2 \rightarrow RO + RO + O_2$
- Termolecular reactions:
 - $OH + SO_2 + M \rightarrow H_2SO_4 + M$
- Equilibria:
 - $NO_2 + NO_3 \rightleftharpoons N_2O_5$
- Phase transfer:
 - Gas-phase \rightarrow aerosol-phase
- Heterogeneous reactions:
 - $2NO_2 + H_2O + \text{surface} \rightarrow HONO + HNO_3$
- ... + more

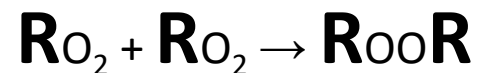
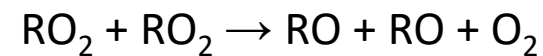
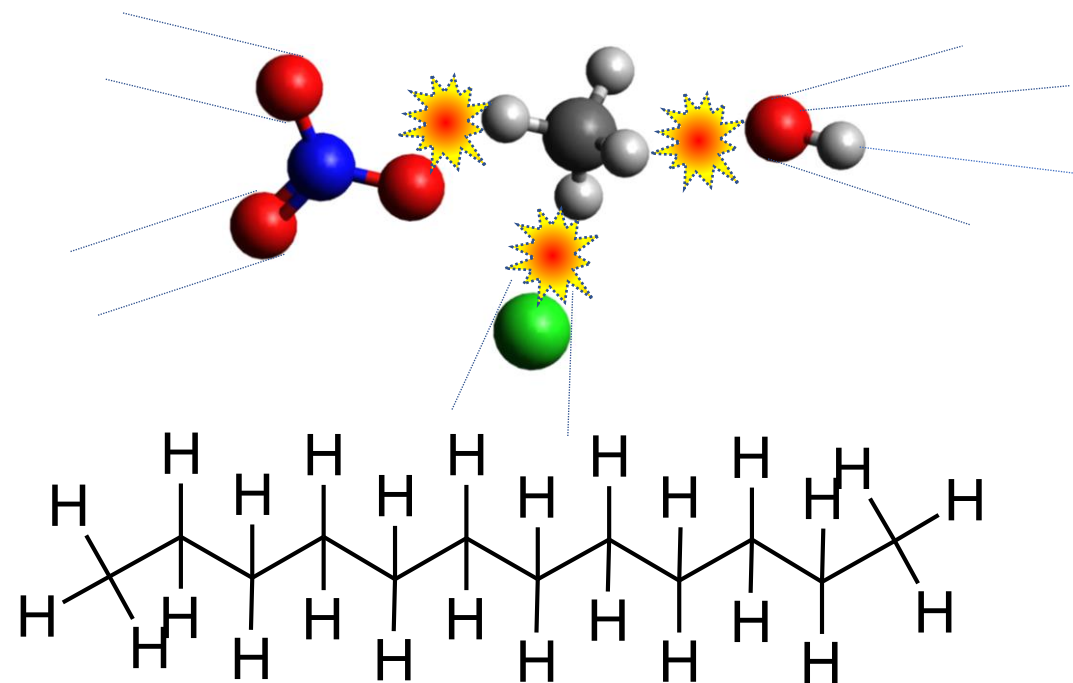
Why we study chemical kinetics

- So, the atmosphere has lots of different chemical reactions that can happen
- Many of these reactions are in competition with each other
- Normally, the faster the rate of reaction, the more important it is
- That is, the more competitive it is



Types of competition

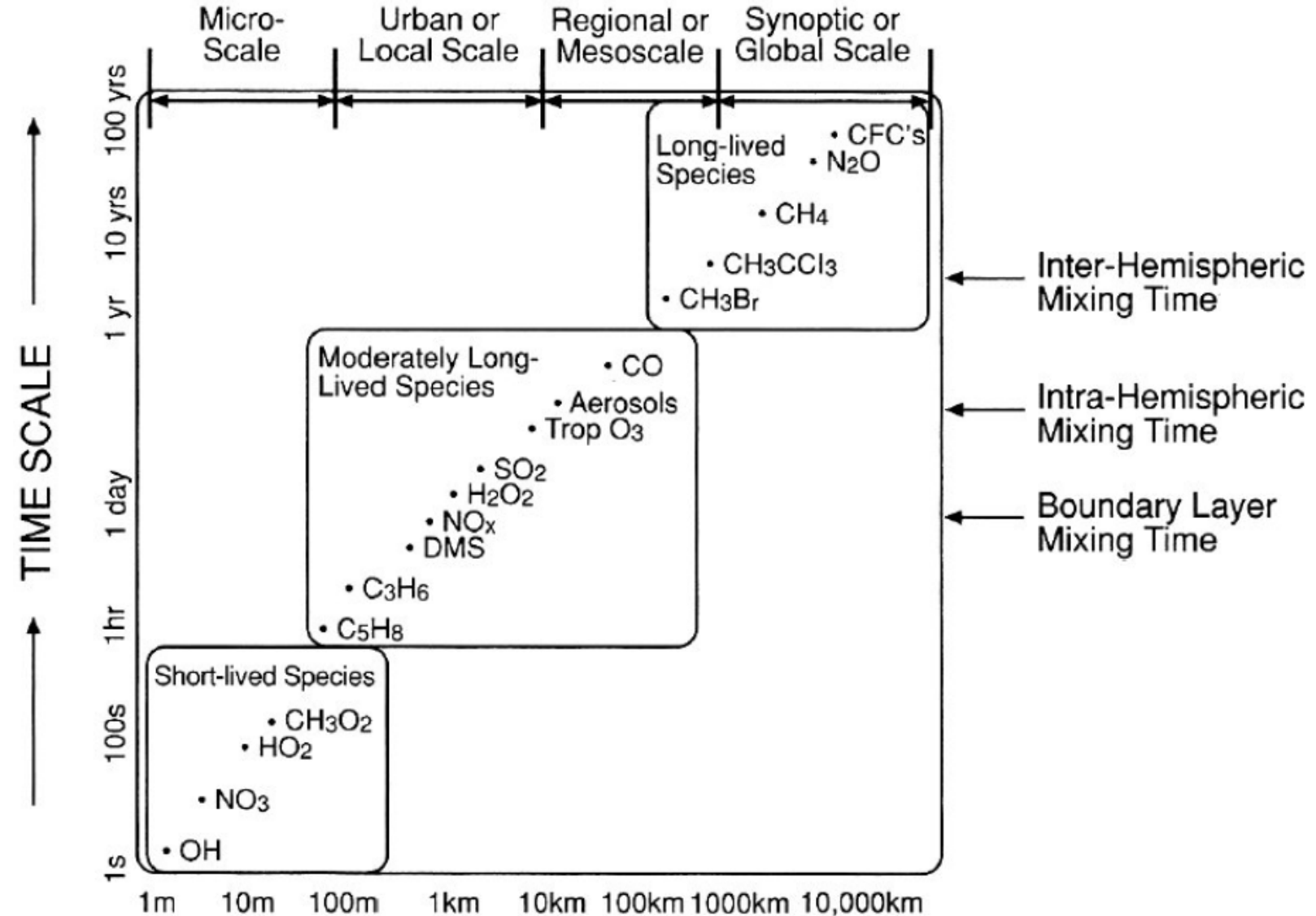
- For a simple compound like methane, we could ask:
which oxidant is most important?
- For more complex compounds, we could ask:
which reactive sites are more important?
- For compounds of a difference size, we could ask:
which mechanism is most important?



Atmospheric lifetime

- Atmospheric chemists often use the lifetime with respect to OH as a general measure of lifetime:

$$\tau = \frac{1}{k[\text{OH}]}$$



Why is the lifetime so important?

- Lifetime is a major control on the distance over which pollution can be transported
- The pollution from one country could affect the air quality of another
- Furthermore, for certain chemicals, vertical transport (and persistence) becomes important (e.g. CFCs, HCFCs)

For example:

$$\text{ODP}_i = \frac{n_{\text{Cl}}}{3} \frac{f_i}{f_{\text{CFC-11}}} \frac{\tau_i}{\tau_{\text{CFC-11}}} \frac{M_{\text{CFC-11}}}{M_i}$$

For example:

$$\text{AGWP}_i(H) = A_i \tau \left(1 - \exp\left(-\frac{H}{\tau}\right) \right).$$

Why is the lifetime so important?

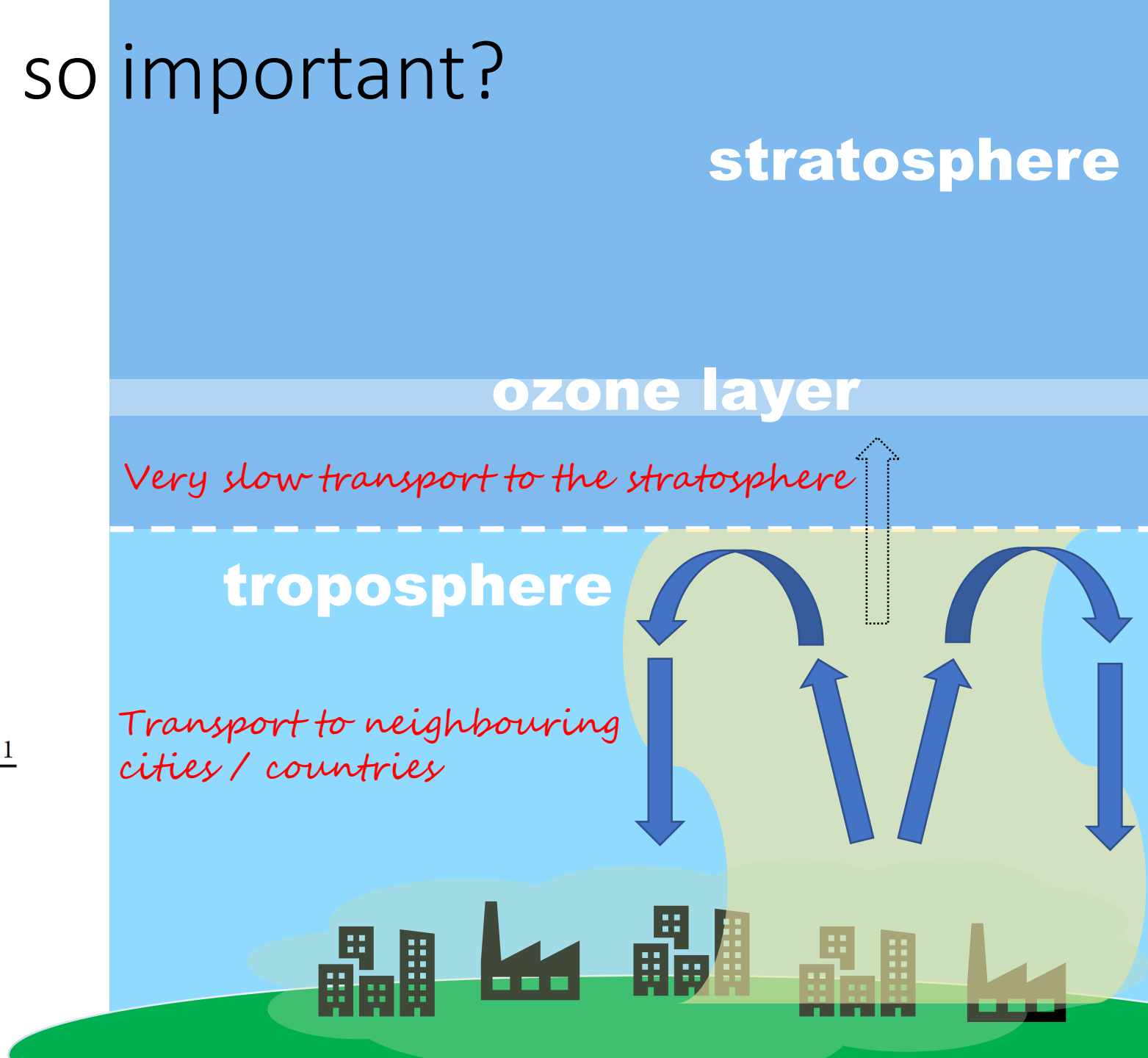
stratosphere

ozone layer

Very slow transport to the stratosphere

troposphere

Transport to neighbouring cities / countries



The total atmospheric lifetime

- Reaction with OH is generally important for destroying pollution
- But there are many other processes that can be important
- Therefore, it is more useful to consider the lifetime as follows:

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} + \frac{1}{\tau_{\text{Cl}}} + \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{hydrolysis}}} + \dots$$

- Also, depending on the location in the atmosphere, individual processes may dominate, e.g. photolysis is faster in the stratosphere, but hydrolysis is very slow, so we can express lifetime as follows:

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_{\text{troposphere}}} + \frac{1}{\tau_{\text{stratosphere}}} + \frac{1}{\tau_{\text{mesosphere}}}$$

Either way, it all depends on k (or J)

$$\tau = \frac{1}{k[\text{OH}]} \quad \tau_{\text{O}_3} = \frac{1}{k[\text{O}_3]} \quad \textit{etcetera ...}$$

$$\tau_{\text{oxidant}} = \frac{1}{k_{\text{oxidant}}[\text{oxidant}]}$$

$$\textit{similarly ...} \quad \tau_{\text{photolysis}} = \frac{1}{J}$$

The rate coefficient, k

- Simple atmospheric chemical reactions are first-order, $A \rightarrow B$ (e.g. unimolecular, photolysis):

$$-\frac{d[A]}{dt} = k[A] \longrightarrow \ln \frac{[A]_0}{[A]_t} = kt$$

Relative concentration change with time (convenient)

- Many atmospheric reactions are bi-molecular and second-order, $A + B \rightarrow C$ (e.g. OH addition):

$$-\frac{d[A]}{dt} = k[A][B] \longrightarrow \frac{1}{[A]_0 - [B]_0} \ln \frac{[A]_t [B]_0}{[A]_0 [B]_t} = kt$$

Absolute concentration change with time (inconvenient)

- Kinetics prefer to work under pseudo-first-order conditions, where:

$$[B] \gg [A] \therefore [B]_0 \approx [B]_t$$

$$-\frac{d[A]}{dt} = k_{obs}[A] \longrightarrow k_{obs} = k \times [B]$$

Changes in concentration and time...

The rate coefficient, k

- But what is k ?
- k is a parameter that describes efficiency
- If k is big, the reaction process is efficient
- If k is small, the reaction process is inefficient
- If k is 100% efficient, then every collision between molecule A and molecule B results in a reaction
- This is known as the “gas kinetic limit” or “collision limit”

The gas kinetic limit

- Begin by considering how fast a gas molecule can move
- Let's consider something simple like N₂ at room temperature:

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8 \times 1.38 \times 10^{-23} (m^2 kg s^{-2} K^{-1}) \times 298 (K)}{3.14 \dots \times 4.65 \times 10^{-26} (kg)}} = 474.7 m s^{-1}$$

- Next, consider how far a molecule travels before it hits another molecule (mean free path):

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P} = \frac{8.314 (m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}) \times 298 (K)}{\sqrt{2}\pi (3.64 \times 10^{-10})^2 (m^2) \times 6.02 \times 10^{23} (1 mol) \times 101325 (Pa)} = 6.898 \times 10^{-8} m$$

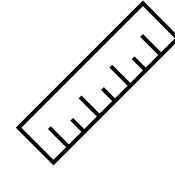
- Now we can calculate how many collisions are happening:

$$Z = \frac{\bar{v}}{\lambda} = \frac{474.7 (m s^{-1})}{6.898 \times 10^{-8} (m)} = 6.88 \times 10^9 s^{-1}$$

- And, if you divide by the number density of 1 atmosphere of gas at room temperature:

$$k = \frac{Z}{n} = \frac{6.88 \times 10^9 (s^{-1})}{2.46 \times 10^{19} (molecule cm^{-3})} = 2.79 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$$

What controls the **size** of k ?



- Some reactions are highly efficient, i.e. \approx gas kinetic limit (e.g. reactions with chlorine and alkenes, $k = 10^{-10}$)
- Others are a lot less efficient (e.g. alkene ozonolysis, $k = 10^{-22}$)
- So, some reactions are a trillion times more efficient than others!
- Where does this inefficiency come from?
- There are several possibilities...

The Arrhenius equation

- Many reactions have an activation energy
- This imparts a temperature dependence:

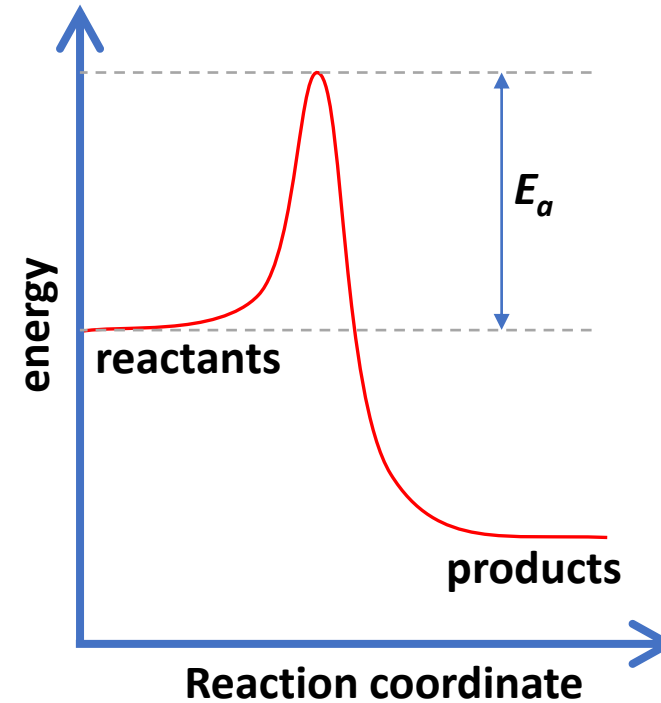
$$k(T) = Z \exp(-E_a/RT)$$

- Other (steric) factors are also important:

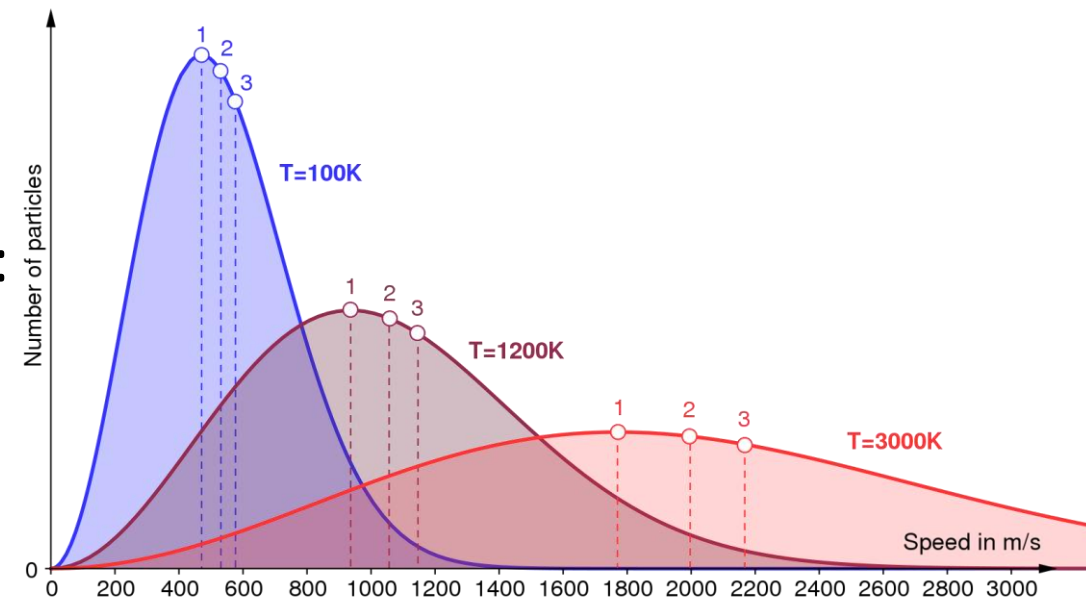
$$k(T) = Z\rho \exp(-E_a/RT)$$

- Leading to the familiar Arrhenius equation:

$$k(T) = A \exp(-E_a/RT)$$



Svante Arrhenius
(1889)



How do we measure kinetic parameters?

Let's consider a bi-molecular reaction ($A + B \rightarrow C$), we generally need three different things:

A. An environment where A and B can react together (a reactor)

- Appropriate temperature/ pressure, absence of secondary chemistry

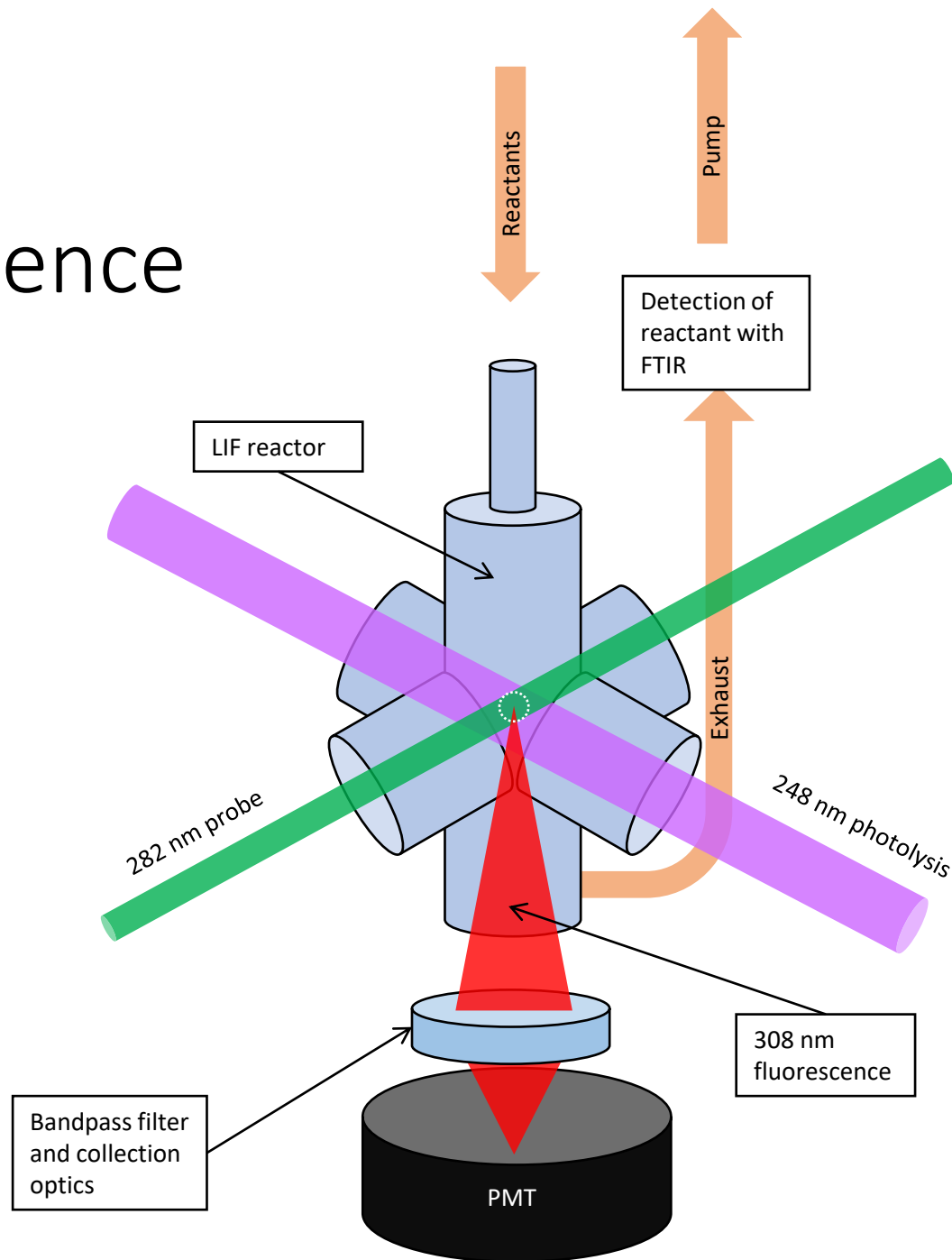
B. An analytical tool to measure (at least one of) A, B or C

- Needs to be sensitive enough, and rapid enough $-\frac{d[A]}{dt} = k_{obs}[A]$

C. A measurement of time

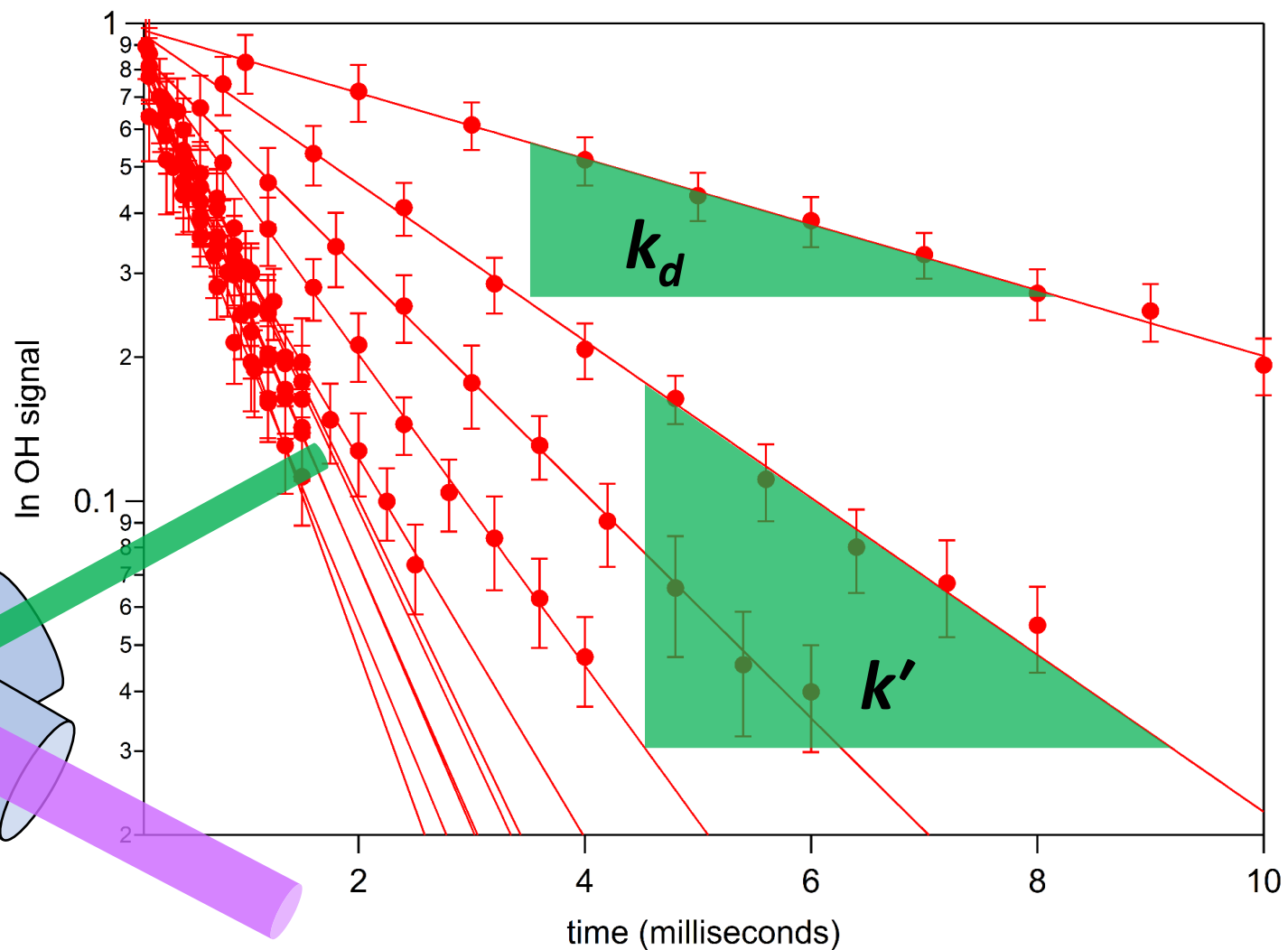
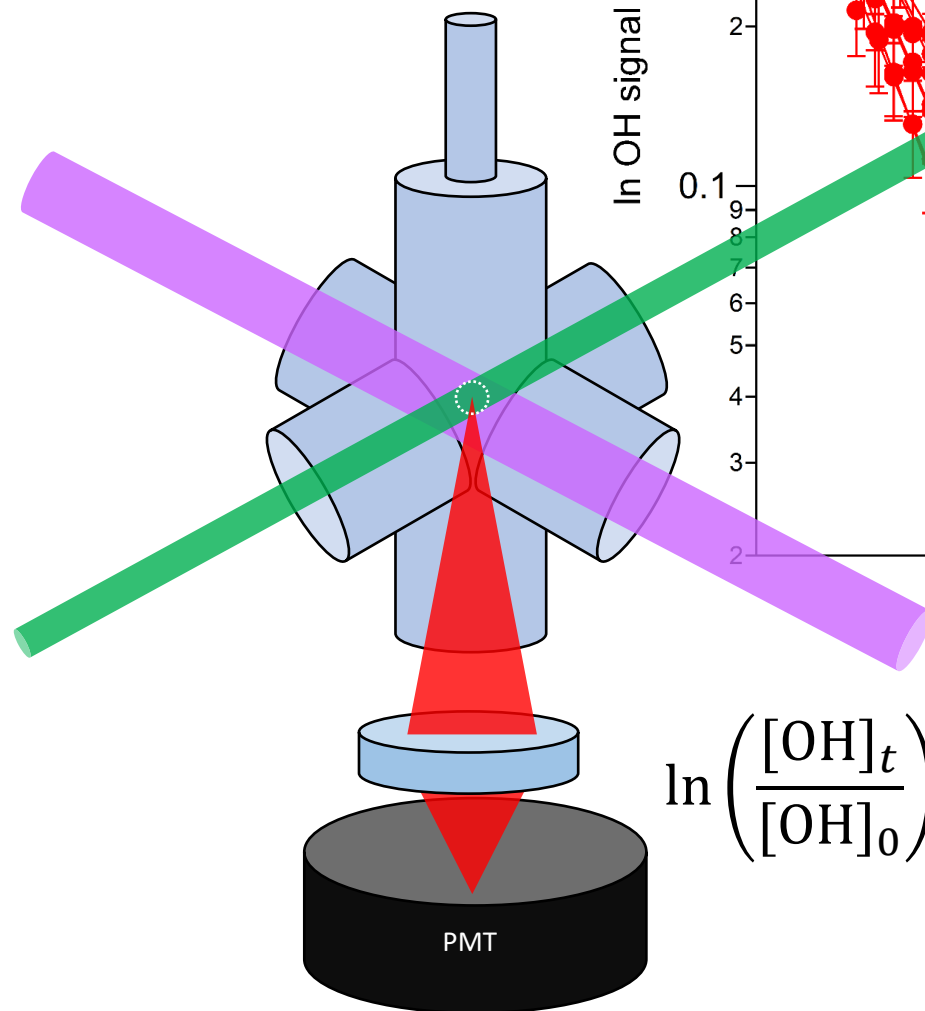
- A way of exposing A to B for a known amount of time $-\frac{d[A]}{dt} = k_{obs}[A]$

Laser Induced Fluorescence

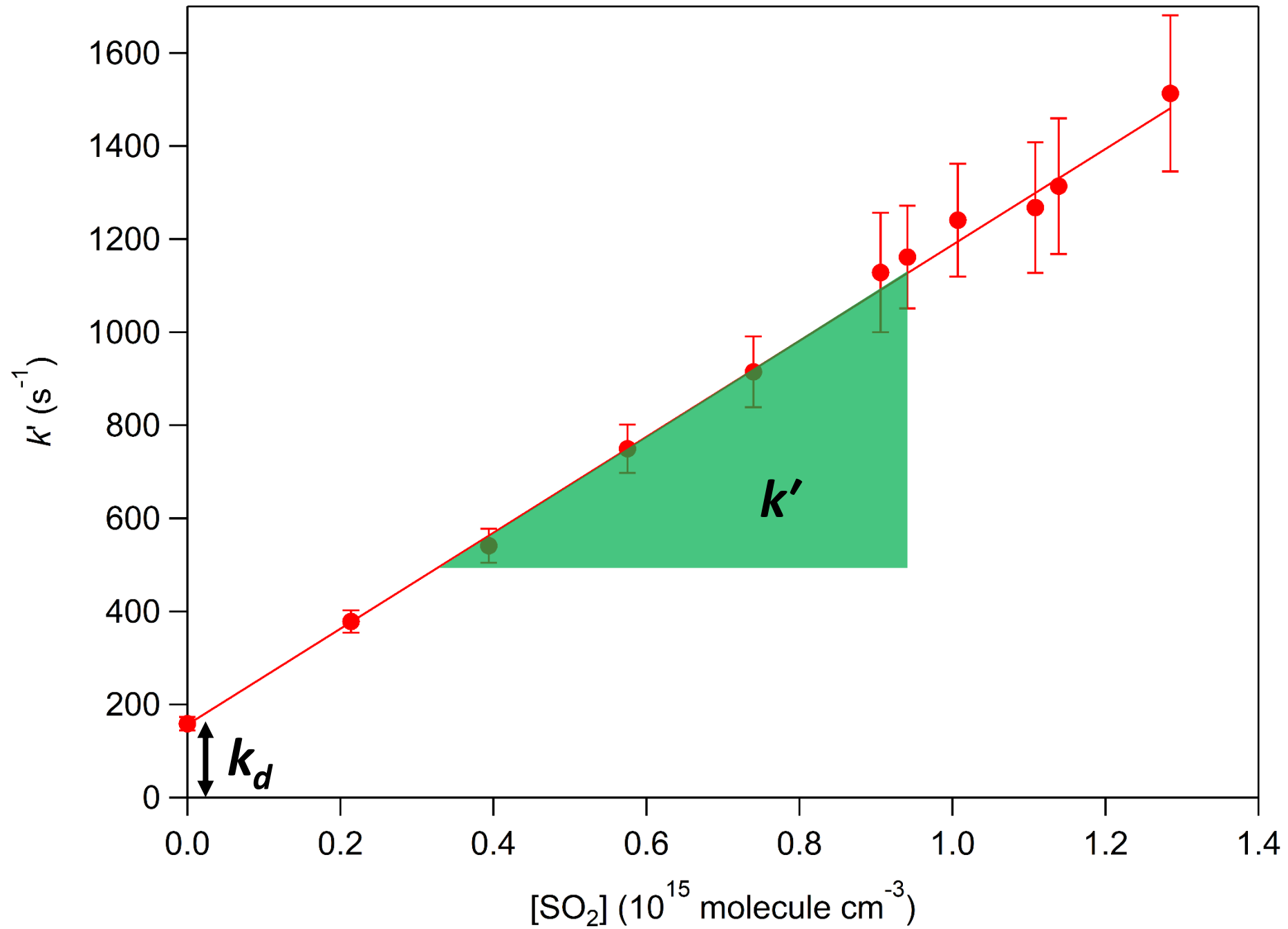


- Temperature range: 220–373 K
- Pressure range: 30–600 Torr
- Bath gases: He, Ar, N₂, O₂
- OH precursors: H₂O₂, HNO₃
- On-line measurement of [SO₂]
- Supporting RR measurements (N₂, Ar, O₂, Air)

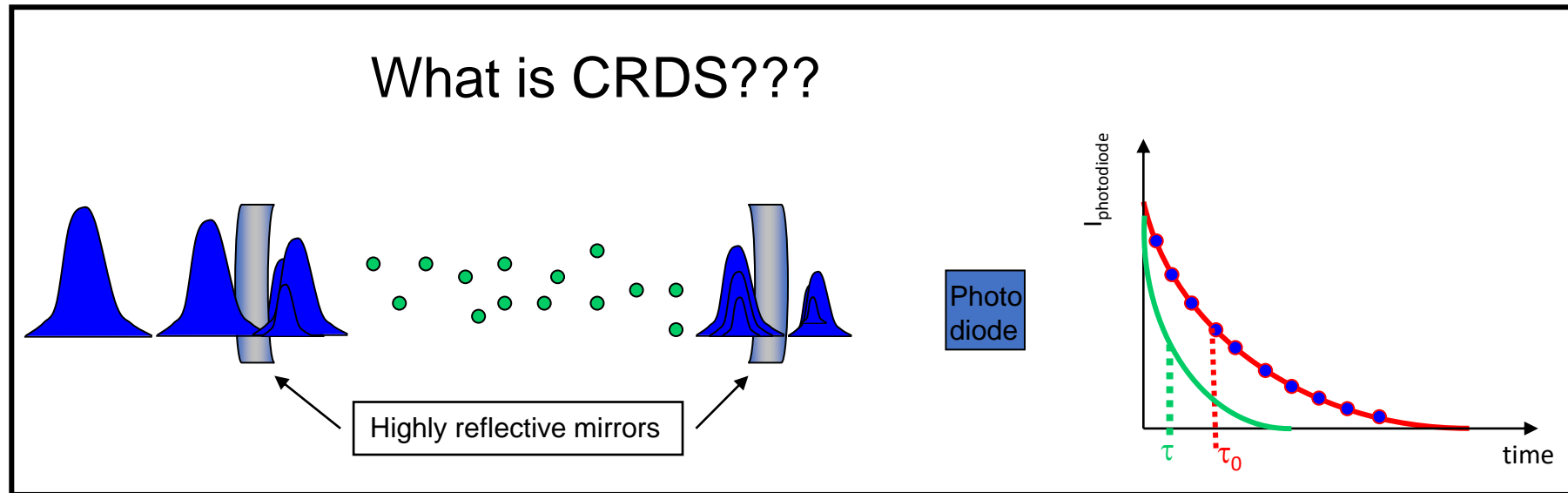
Laser Induced Fluorescence



$$\ln \left(\frac{[\text{OH}]_t}{[\text{OH}]_0} \right) = \ln \left(\frac{S_t}{S_0} \right) = -(k[\text{reactant}] + k_d)t = -k't$$



Laser photolysis coupled to CRDS

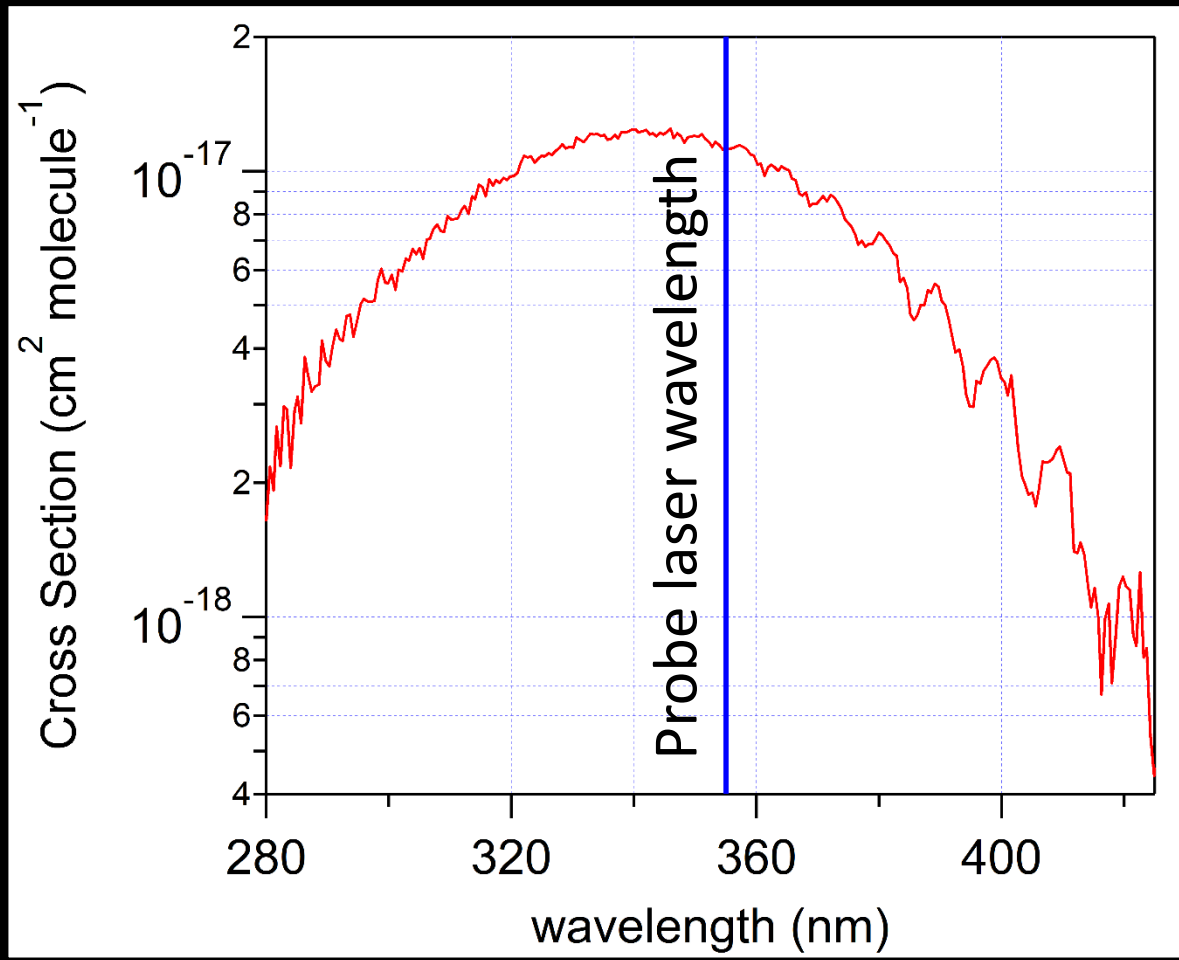
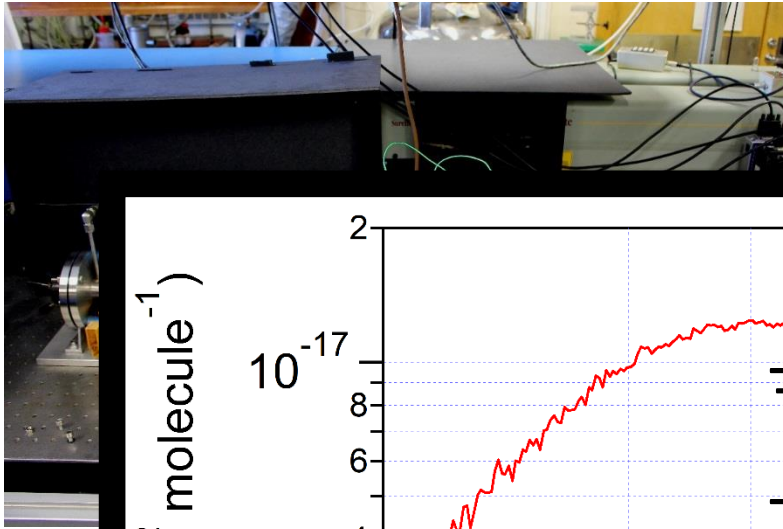
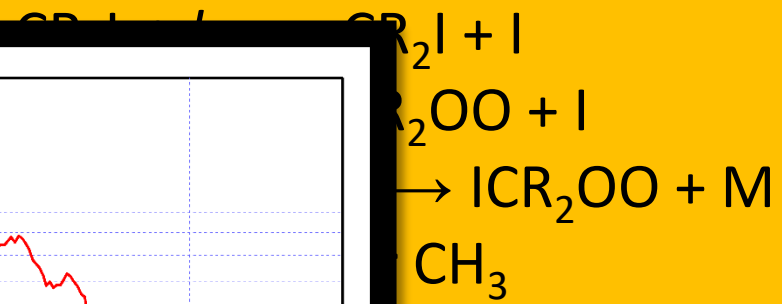


$$\tau_0 = \frac{L}{c(1-R)}$$

$$\tau_{abs} = \frac{L}{c\{(1-R) + [abs]\sigma_{abs}L\}}$$

$$[abs]\sigma_{abs} = \frac{1}{c} \left(\frac{1}{\tau_{abs}} - \frac{1}{\tau_0} \right)$$

Convenient chemistry

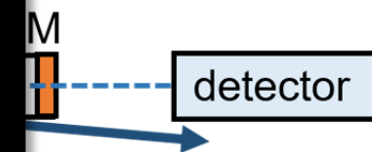


355 nm probe light

T range:
 P range:
 Ring-down
 Reaction

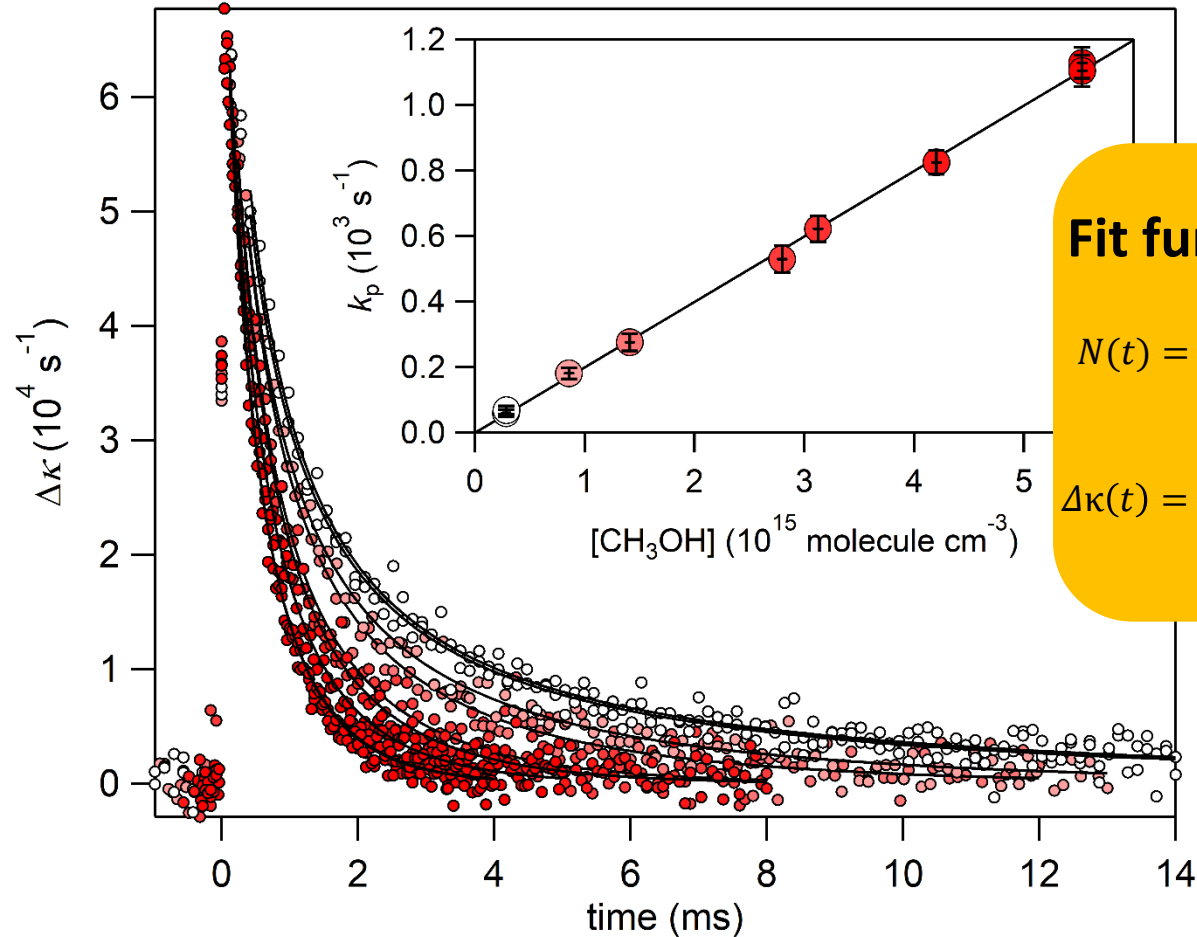
$[Cl]_0: \sim 2 \times 10^{12}$ (molec. cm⁻³)

and gas



mirror with N₂ purge
 thermocouple
 pressure gauge

heater

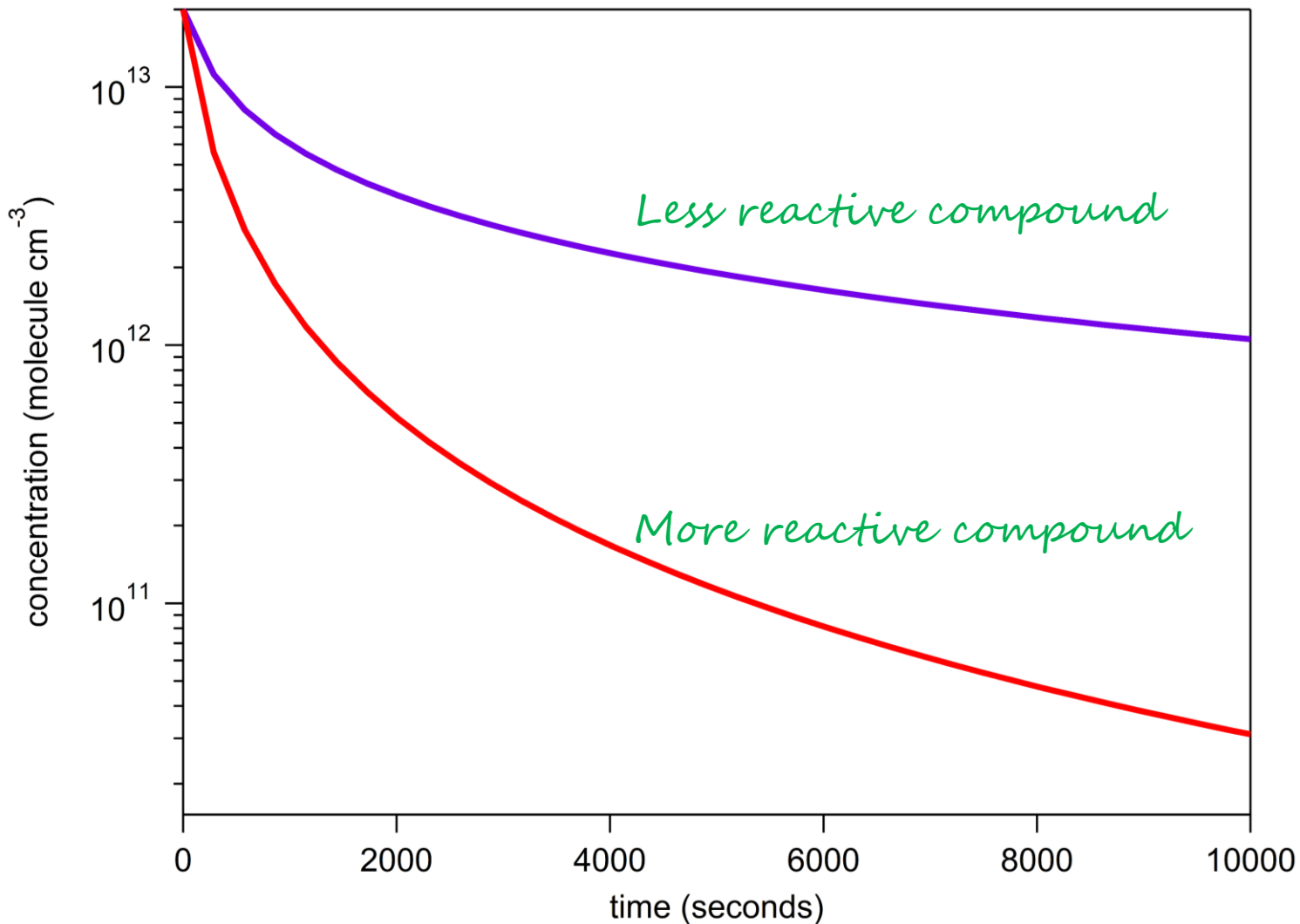


Fit function: $\frac{dN}{dt} = -2k_{obs}N^2 - k_pN$

$$N(t) = \frac{k_2N(t_0)}{k_p e^{k_p t} - 2k_{obs}N(t_0) + 2k_{obs}N(t_0)e^{k_p t}}$$

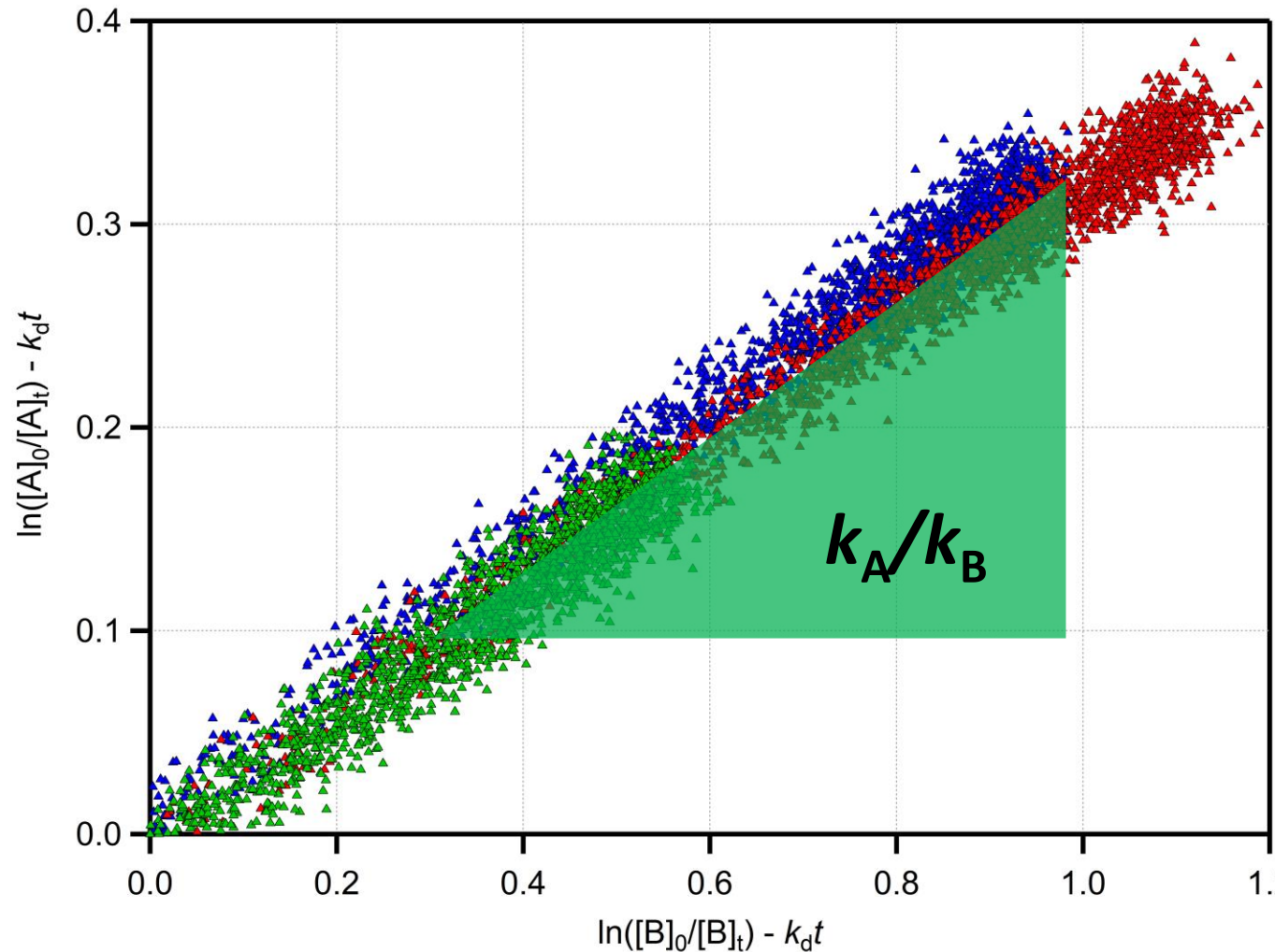
$$\Delta\kappa(t) = \frac{k_p}{\frac{k_p}{\Delta\kappa(t_0)} e^{k_p t} - (k') \left(\frac{2L}{cd}\right) + (k') \left(\frac{2L}{cd}\right) e^{k_p t}}$$

Relative rate kinetics



- Another approach is to use the relative rate approach
- Here we introduce two compounds that are allowed to react simultaneously:
$$A + OH \rightarrow \text{product}$$
$$B + OH \rightarrow \text{product}$$
- So, if we know the reactivity of B (for example), then we can deduce that of A

Relative rate kinetics



- This is done with the relative rate approach:

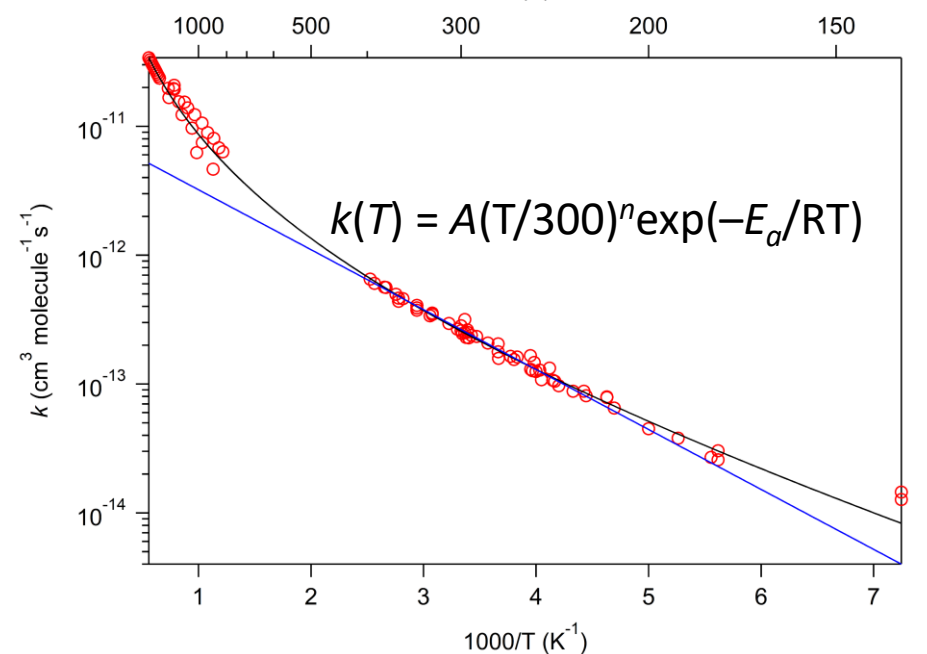
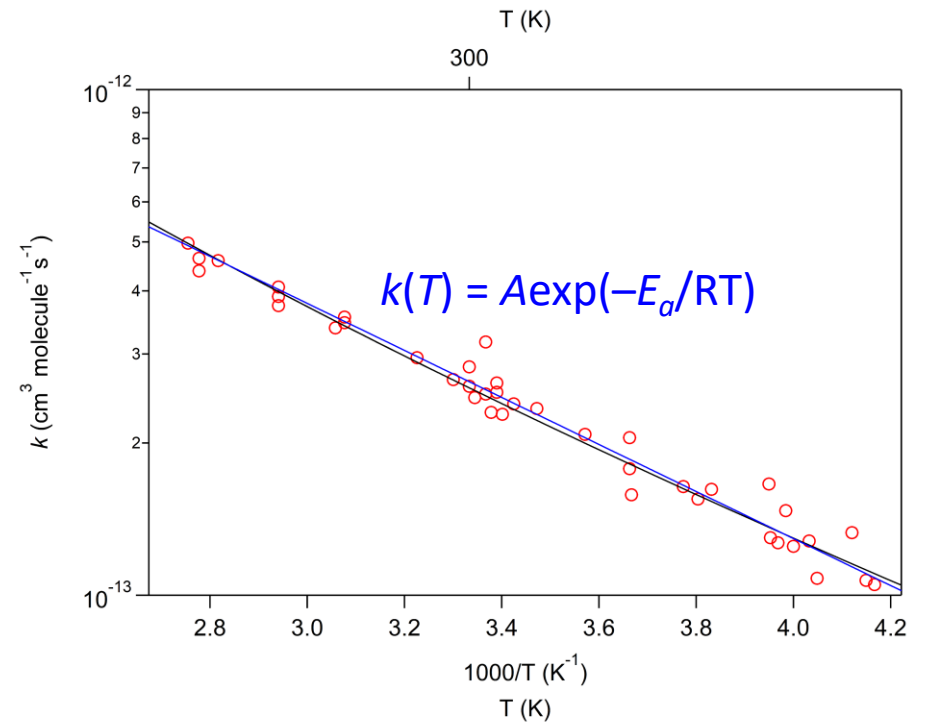
$$\ln\left(\frac{[A]_0}{[A]_t}\right) - k_d t = \frac{k_A}{k_B} \ln\left(\frac{[B]_0}{[B]_t}\right) - k_d t$$

- This can be very precise and effective, but it is limited by the accuracy of the reference

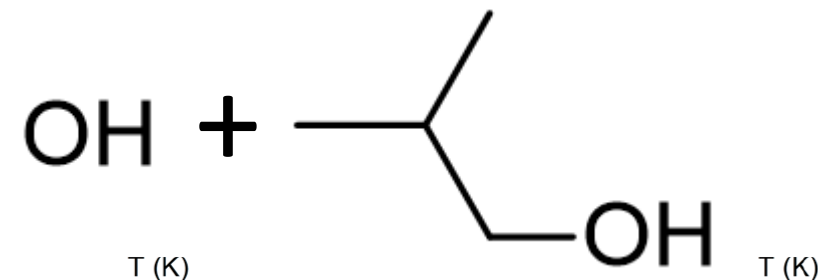


T-dependence of k

- Many reactions are temperature dependent
- And over a small temperature range, they may obey the **Arrhenius equation**
- But over larger ranges, we observe curvature
- And this curvature can be described by the **modified Arrhenius equation**
- This is referred to as non-Arrhenius behaviour

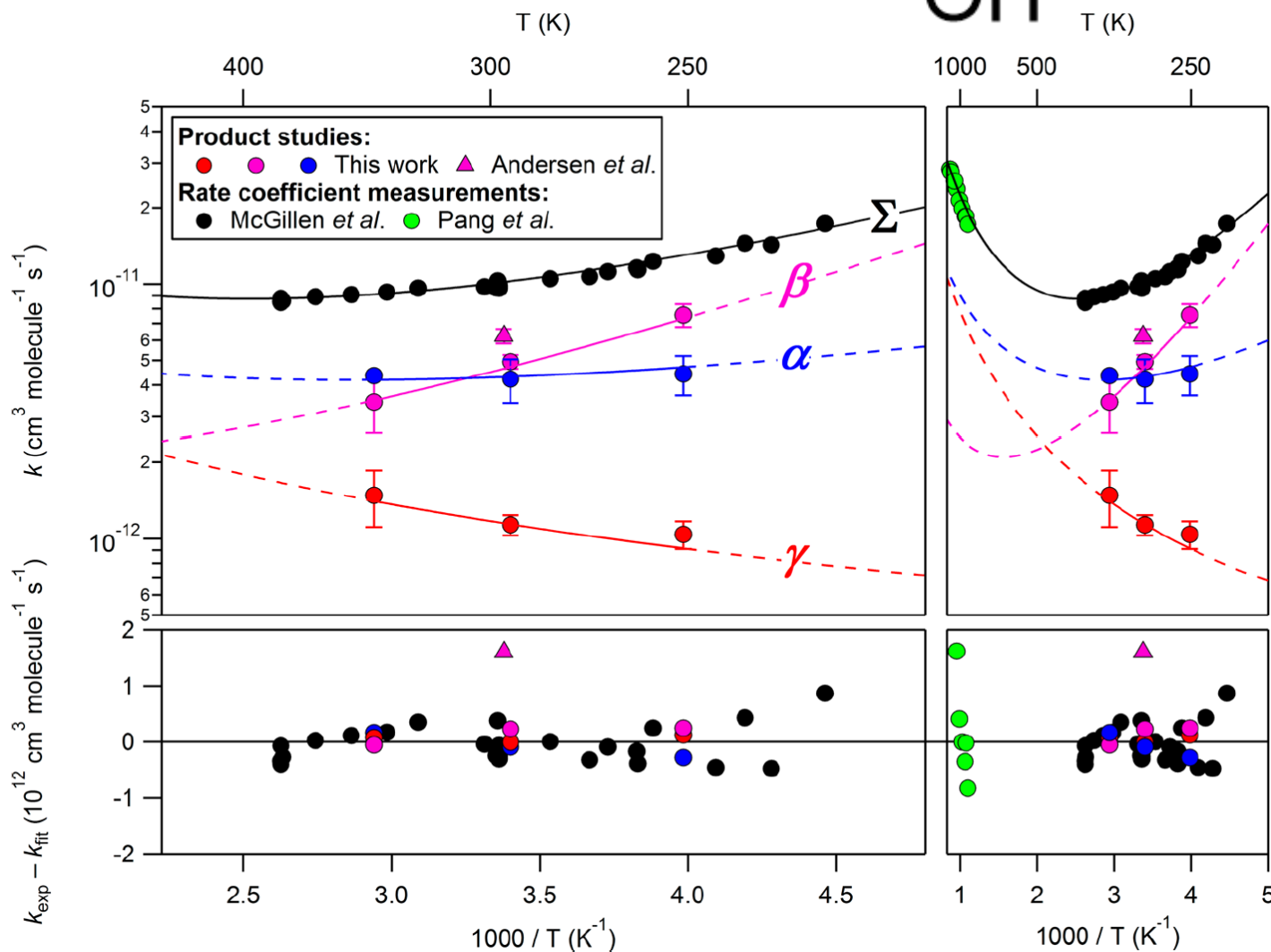


Non-Arrhenius behaviour



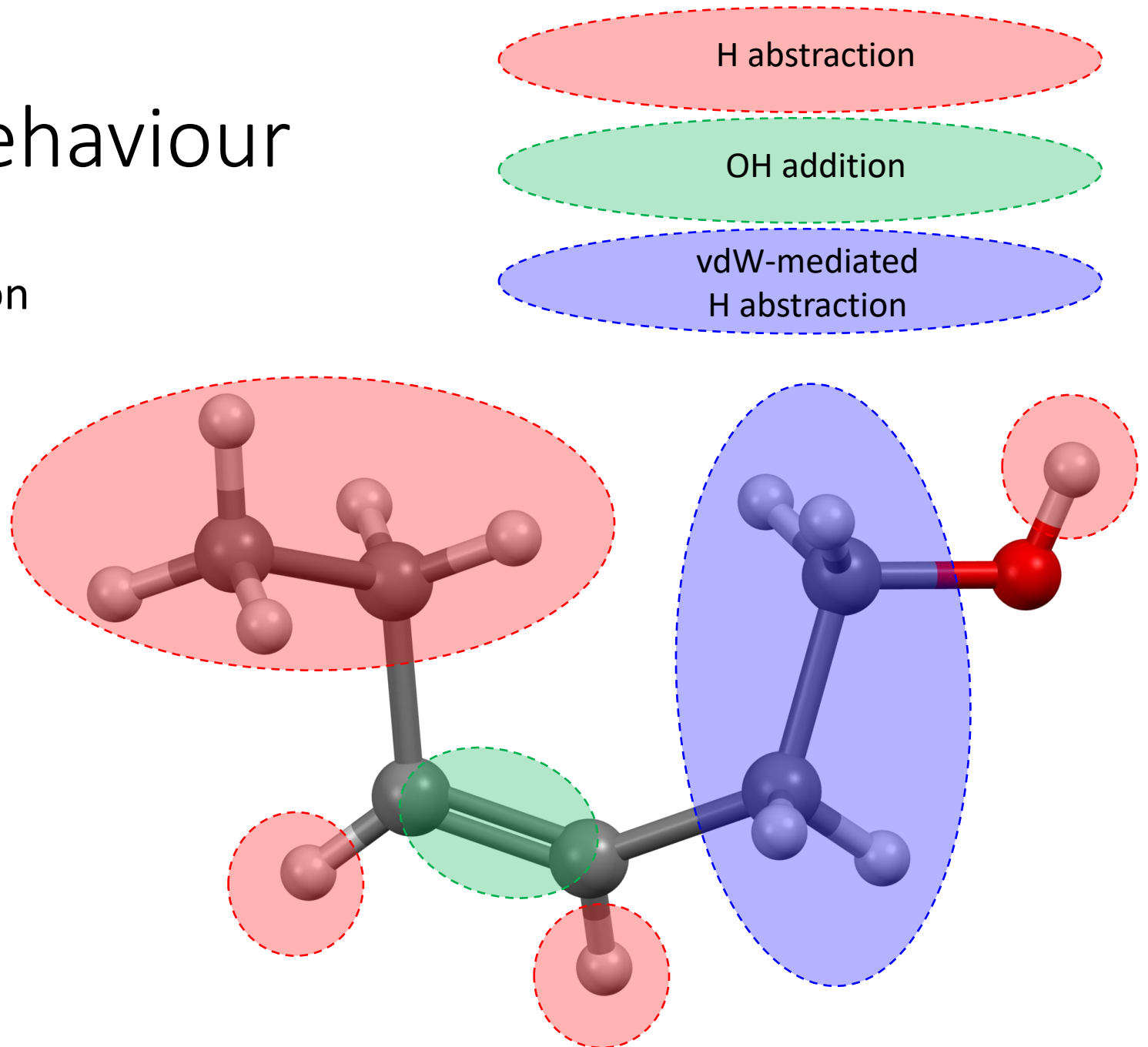
- Several reasons for this:
- Multiple (*i*) reactions sites, each with their own different T-dependence
- Since the total reaction rate is the sum of each:

$$k_{\text{total}}(T) = \sum_i \kappa_i A_i e^{-E_i/RT}$$



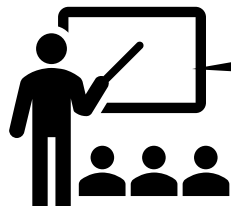
Non-Arrhenius behaviour

- A typical atmospheric emission such as *cis*-3-hexenol possesses **several reaction sites**
- These sites react through **several mechanisms**, which respond differently to temperature changes
- Some sites have a positive T-dep, some sites have a negative T-dep, some sites have positive and negative T-dep
- Wait... negative T-dep?



Negative temperature-dependence of k

- Remember what I said earlier?
- Well, it is true, but it isn't the whole truth...



The Arrhenius equation

- Many reactions have an activation energy
- This emparts a temperature dependence:

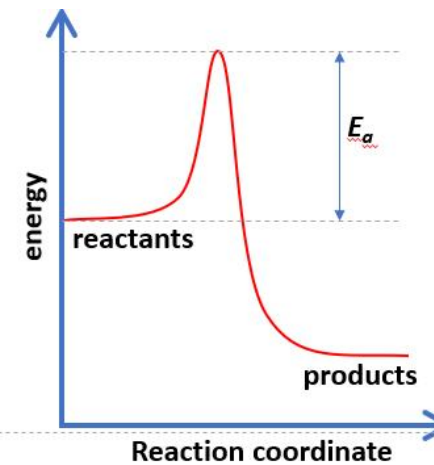
$$k(T) = Z \exp(-E_a/RT)$$

- Other (steric) factors are also important:

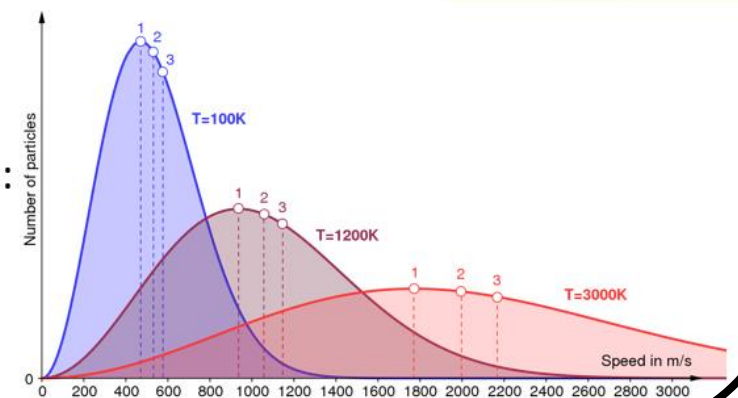
$$k(T) = Zp \exp(-E_a/RT)$$

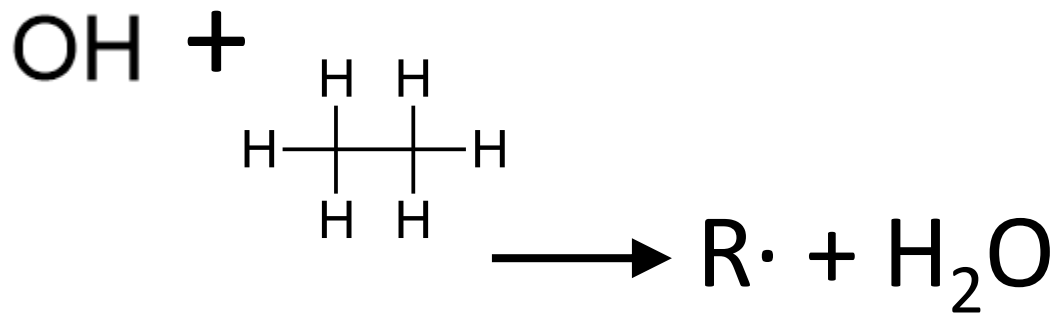
- Leading to the familiar Arrhenius equation:

$$k(T) = A \exp(-E_a/RT)$$

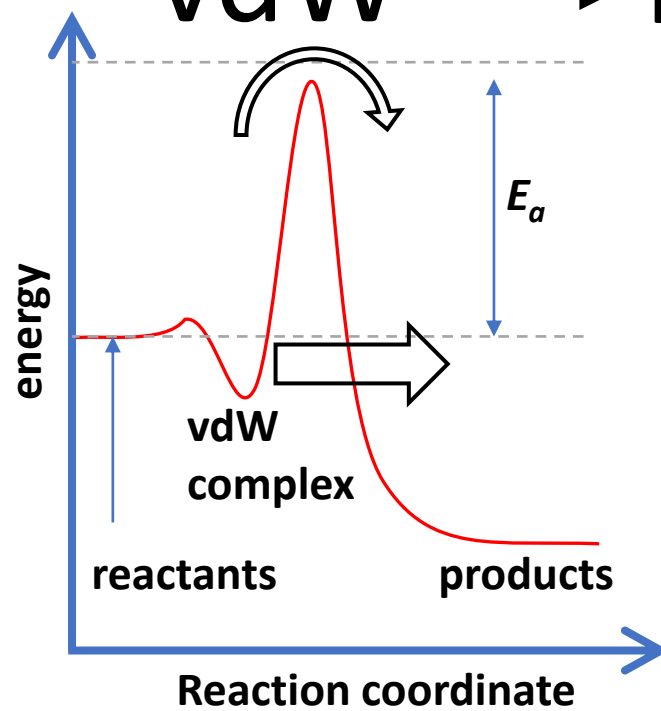
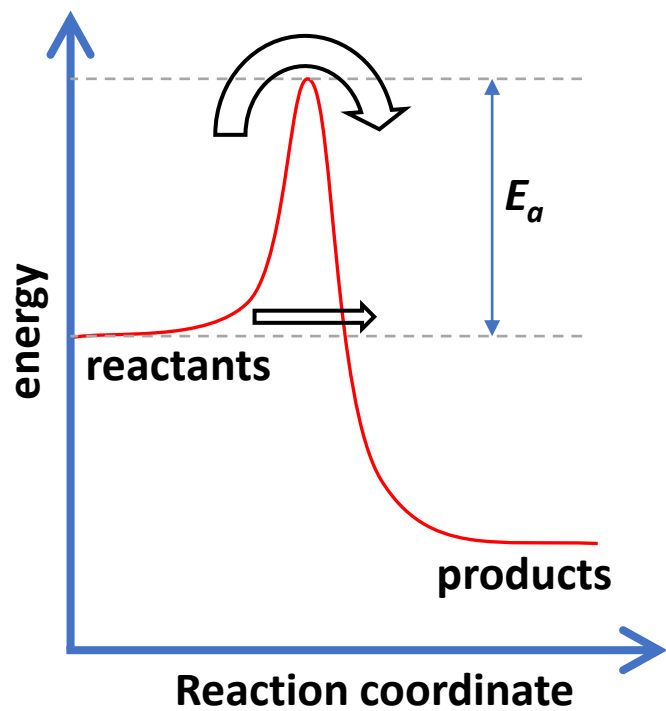
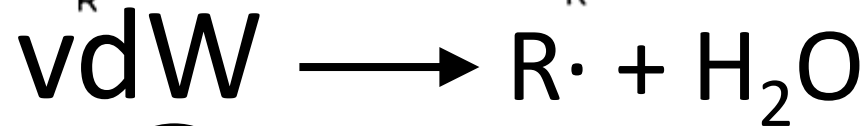
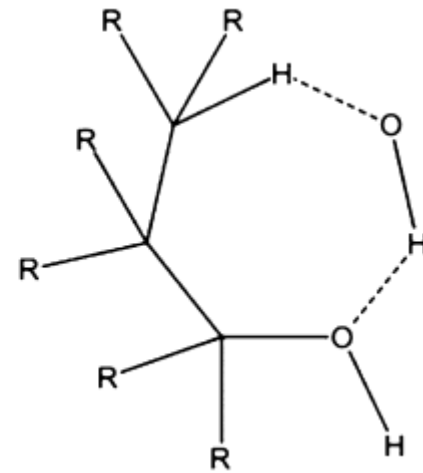
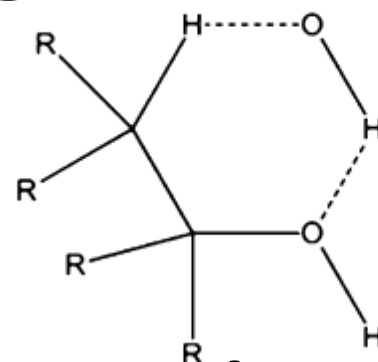
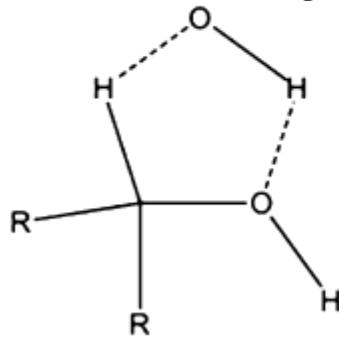


Svante Arrhenius
(1889)



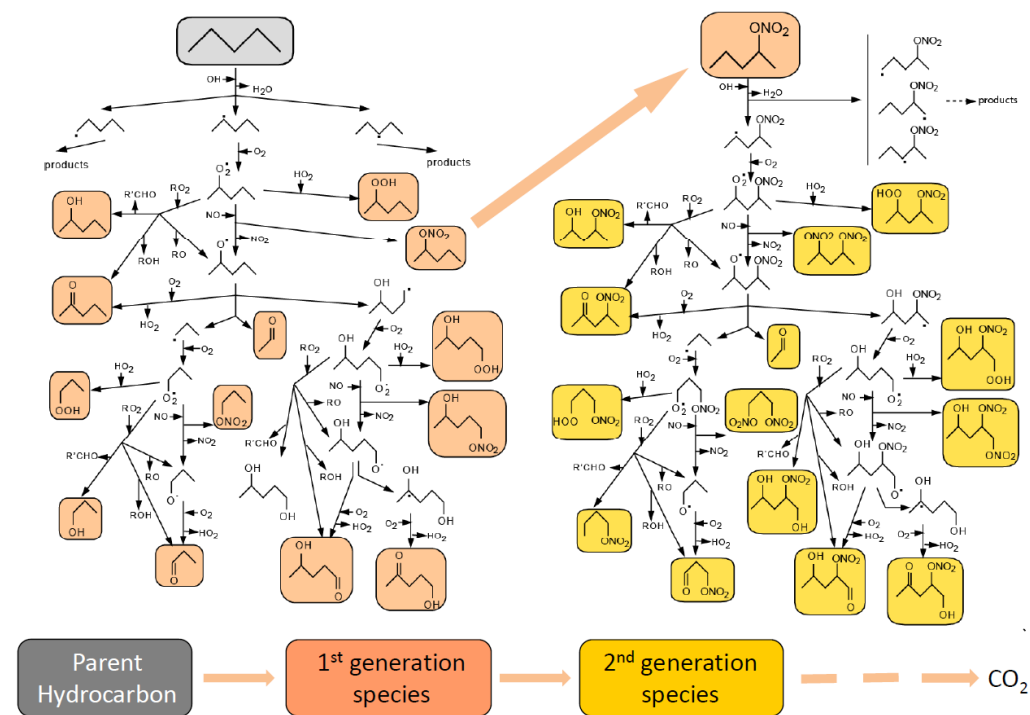


OH + oxygenate



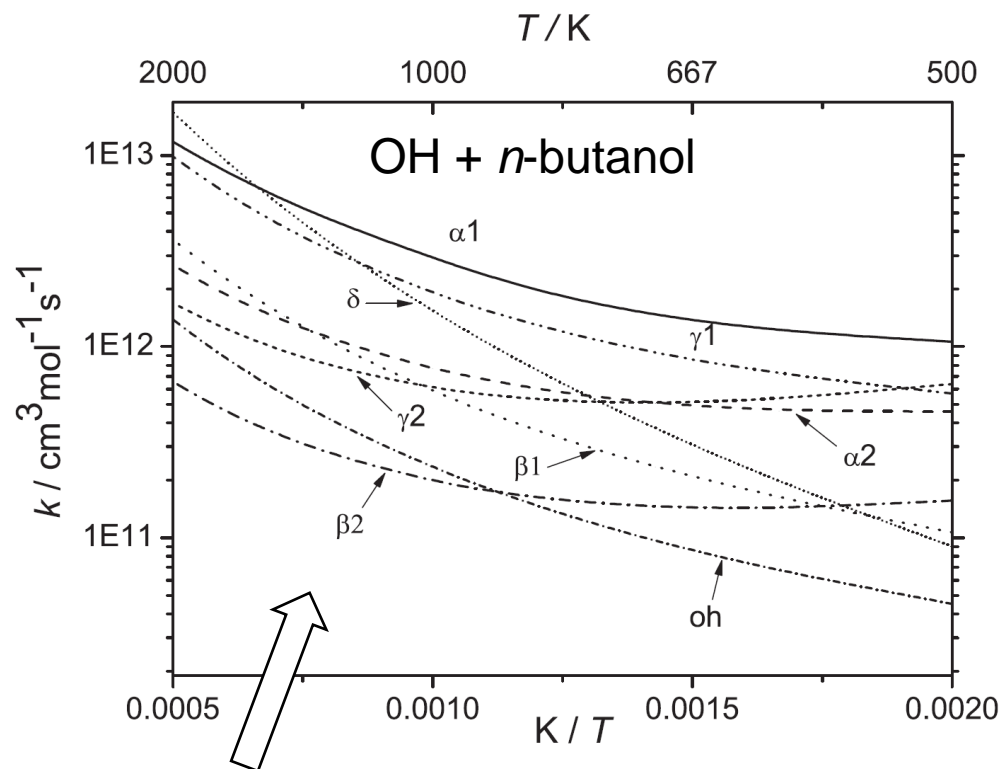
Negative temperature-dependence of k

- We see negative temperature dependence for many atmospheric reactions
- Atmospheric chemistry transforms reduced molecules into oxygenated molecules
- This is an opportunity for **van der Waals complexes** to form
- In fact, non-Arrhenius behaviour is not exceptional, it is common



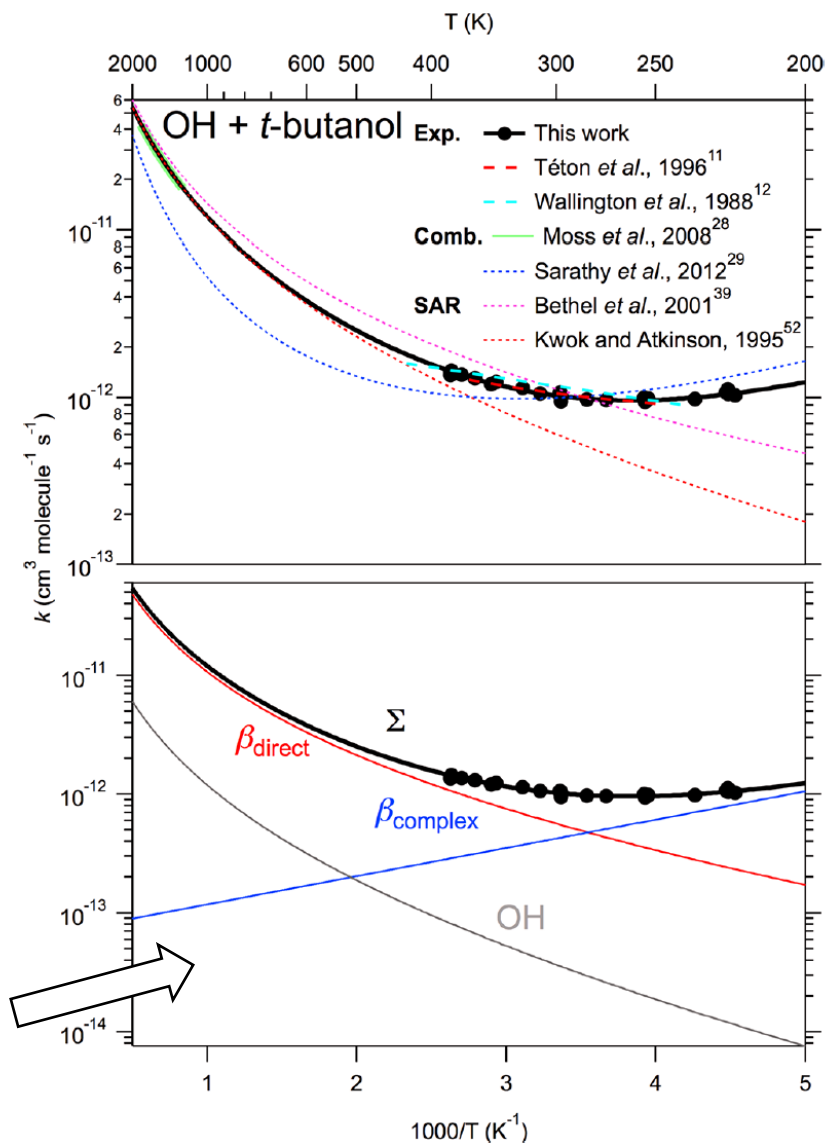
Almost all atmospheric degradation products are oxygenated

Non-Arrhenius behaviour



Zhou *et al.* (2011) identified 8 reaction channels in a reaction that possesses 5 reaction sites

McGillen *et al.* (2013) used 3 reaction channels to describe a reaction that possesses 2 reaction sites



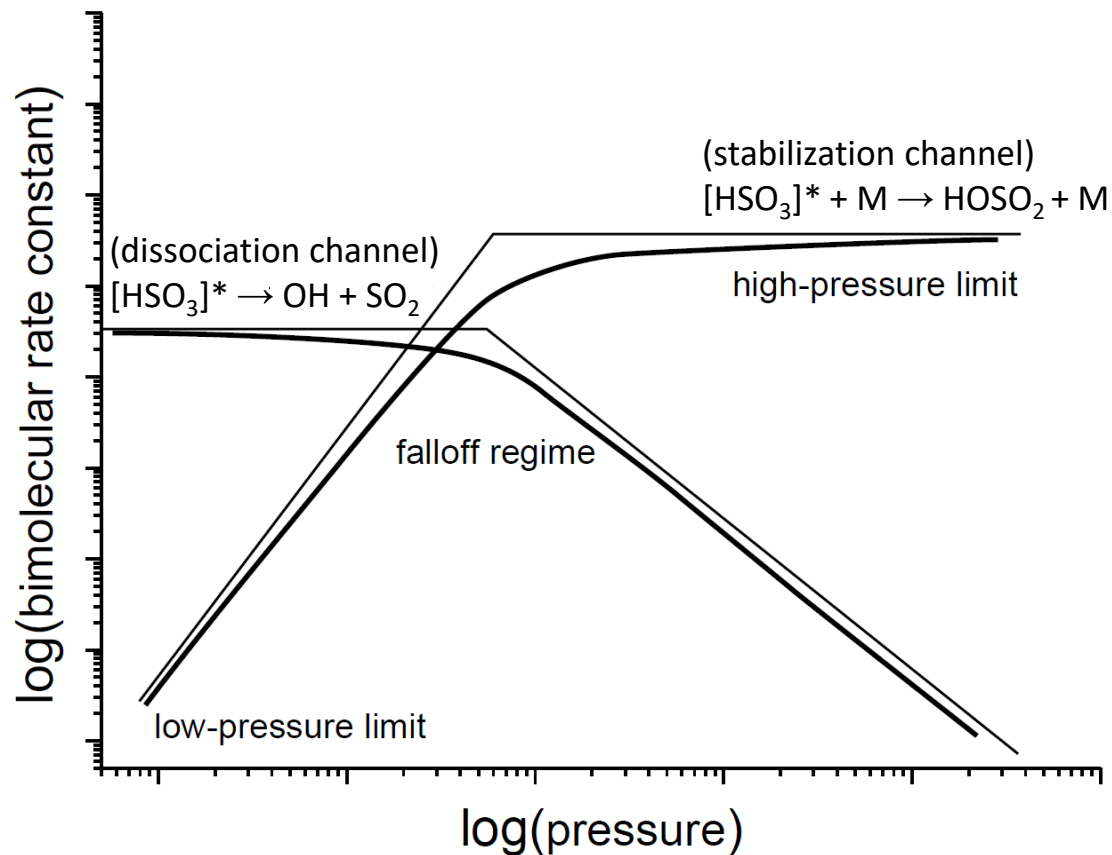
Pressure-dependence of k

- There are several very important reactions in the atmosphere that exhibit pressure dependence
- Pressure dependence in atmospheric reactions (mostly) involves energy transfer with the N_2 and O_2
- These are referred to as M, a third body that doesn't participate direction in a reaction:

For example: $SO_2 + OH \rightleftharpoons [HOSO_2]^* + M \rightarrow HOSO_2 + M \rightarrow \rightarrow H_2SO_4$

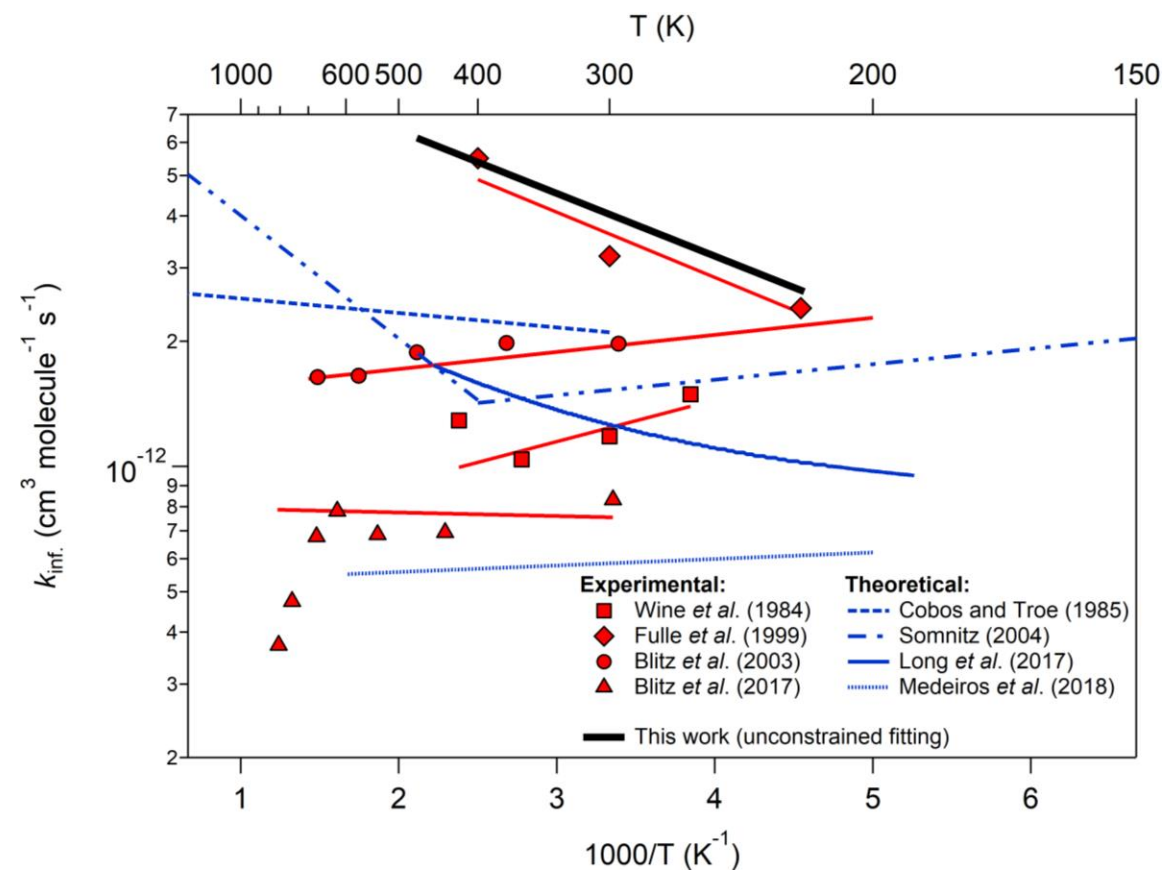
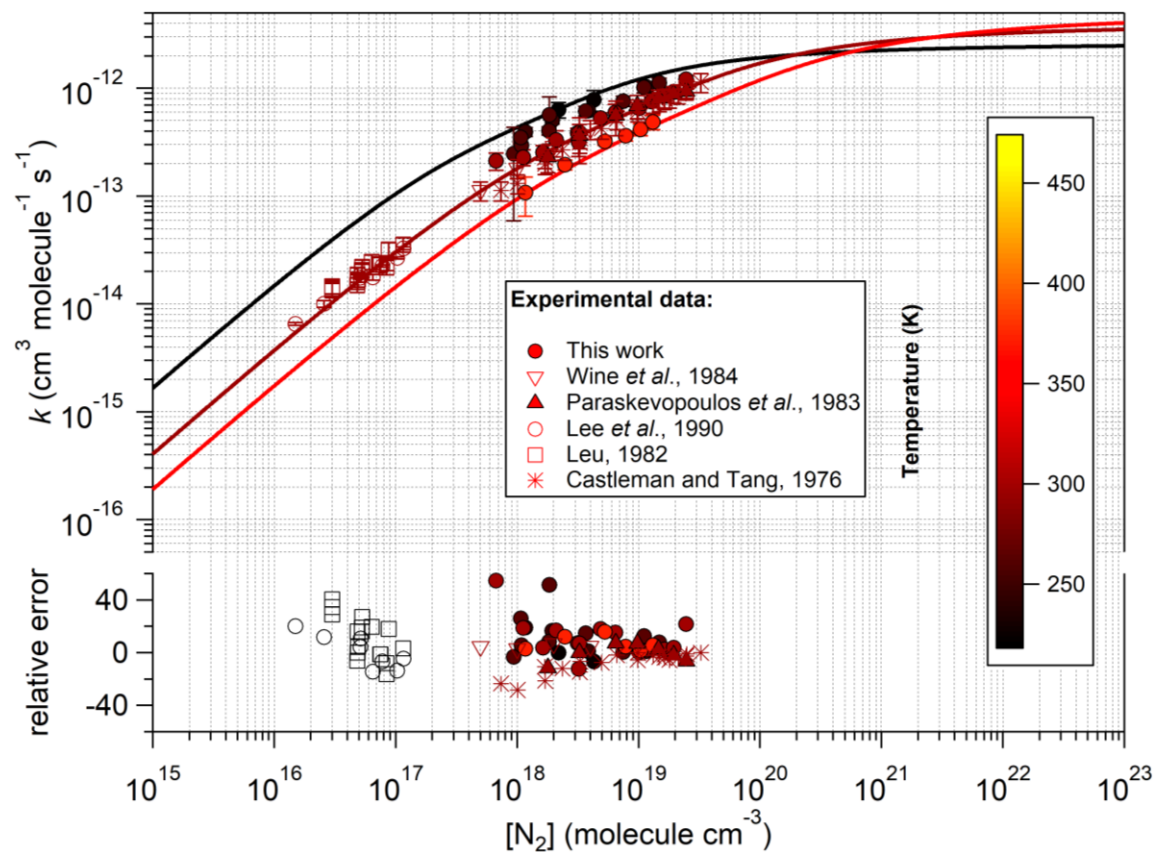
- This is a competition: can $[HOSO_2]^*$ collide with M before it falls apart?
- Therefore, this reaction depends on $[M]$ (\propto pressure)

kinetics in the fall-off regime

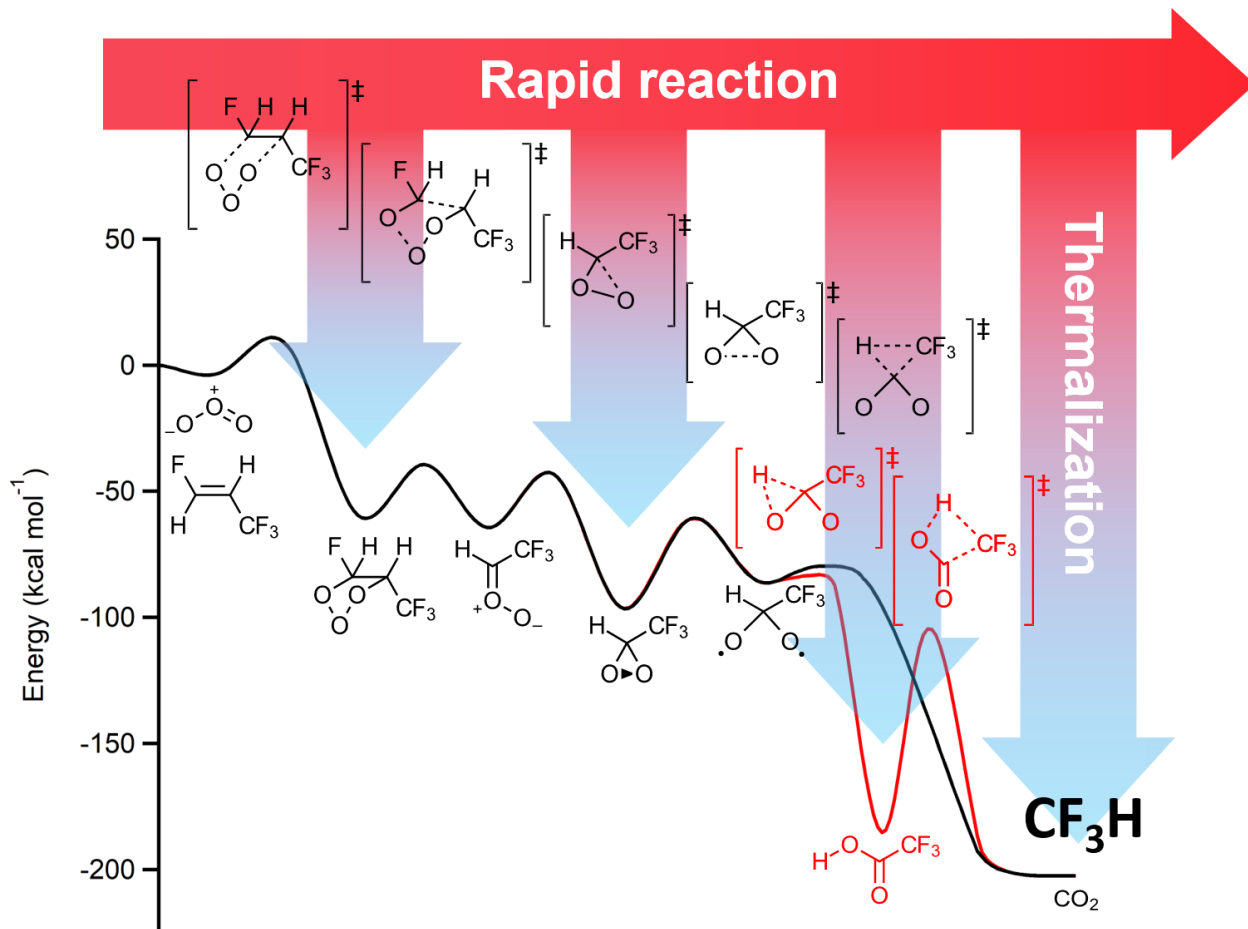


- Where atmospheric pressure dependence is important, reactions are usually in the fall-off region
- At some point, k cannot get any larger, it has reached its high-pressure limit (k_∞)
- The onset of k_∞ can vary widely <mBar – 100s of Bar
- This depends of the stability of the intermediate

P- and T-dependence in OH + SO₂



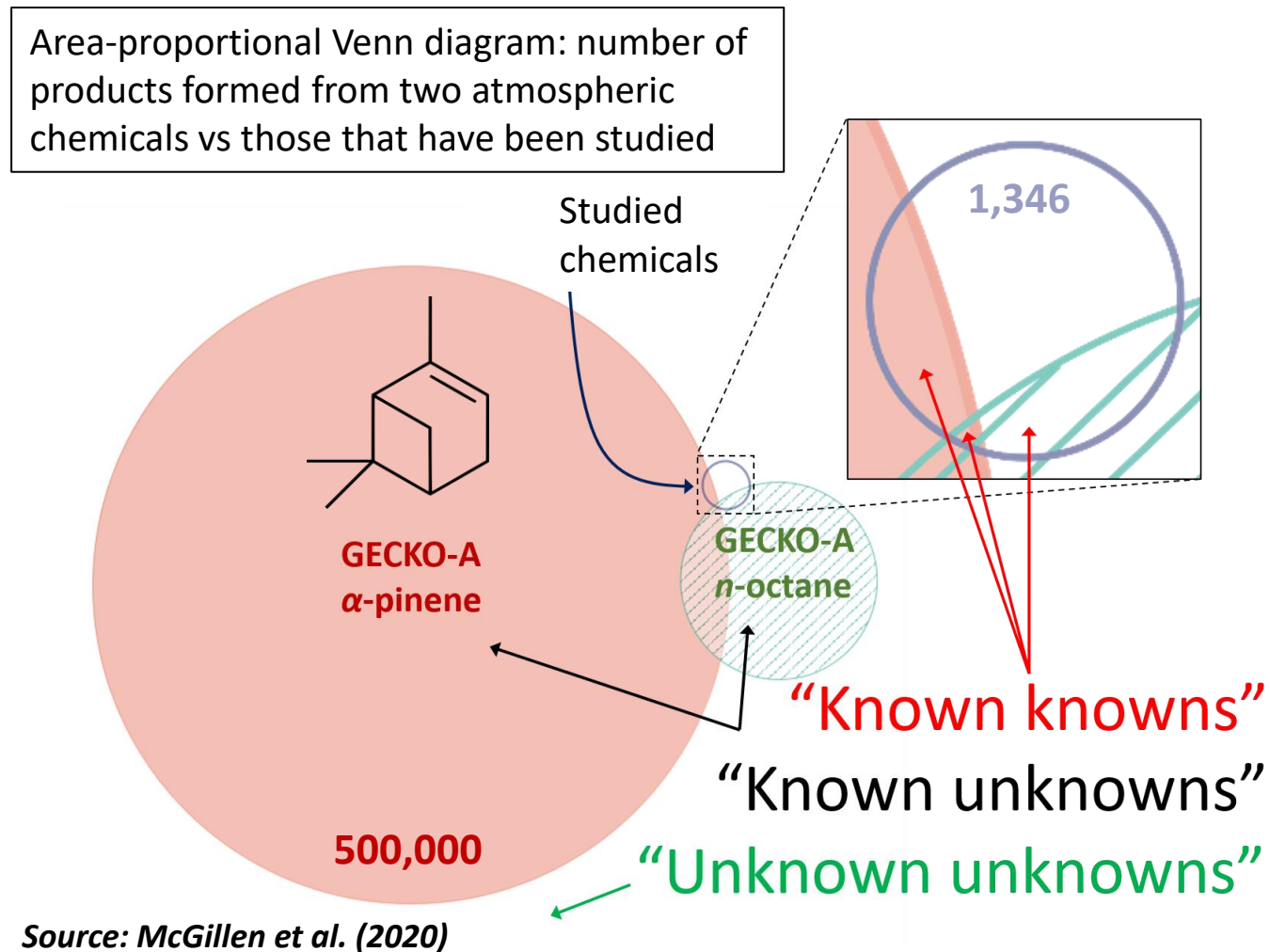
Pressure dependence in ozonolysis



- Ozonolysis is a unique chemical system with a large number of local minima on the PES
- There is a cascade of intermediate species, which are losing energy by colliding with M
- It becomes a race to the bottom of the potential energy surface

Estimating k

- I have talked a lot about measuring k so far
- But measuring k is often very difficult and time-consuming
- Yet there are many reactions rates that we would like to know
- This is generally done by parameterizing aspects of molecules that control reactivity
- These are the structure-activity relationships (SARs)

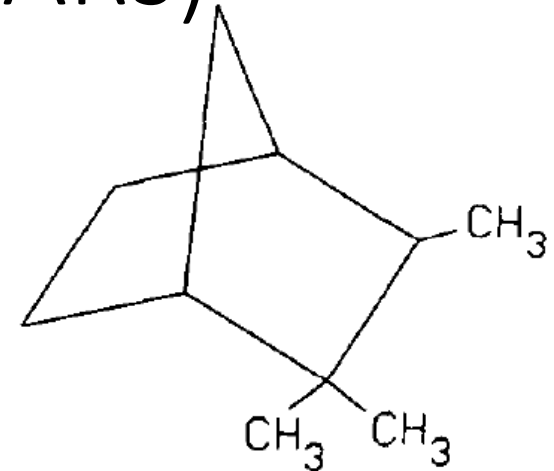


Structure-activity relationships (SARs)

- There are many types of SARs that can be used
- The most popular approach is the group-additivity method
- This method makes use of the idea that the observed k is the summation of all reaction channels:

$$k_{\text{total}}(T) = \sum_i \kappa_i A_i e^{-E_i/RT}$$

- This has the advantage of providing estimates for product branching ratios
- This is ideal for chemical models, where we want to know the lifetime of a chemical, but also the secondary pollutants that are formed



$$\begin{aligned}
 k_{\text{total}} = & \{ 2k_{\text{sec}} F(-\text{CH}_2-) F(>\text{CH-}) F_5 F_6 \\
 & + k_{\text{tert}} [F(-\text{CH}_2-)]^2 F(>\text{CH-}) F_5 F_5 F_6 \\
 & + k_{\text{tert}} [F(-\text{CH}_2-)]^2 F(>\text{C}<) F_5 F_5 F_6 \\
 & + k_{\text{sec}} [F(>\text{CH-})]^2 F_5 F_5 \\
 & + k_{\text{tert}} F(>\text{C}<) F(>\text{CH-}) F(-\text{CH}_3) F_5 F_6 \\
 & + 2k_{\text{prim}} F(>\text{C}<) + k_{\text{prim}} F(>\text{CH-}) \}
 \end{aligned}$$

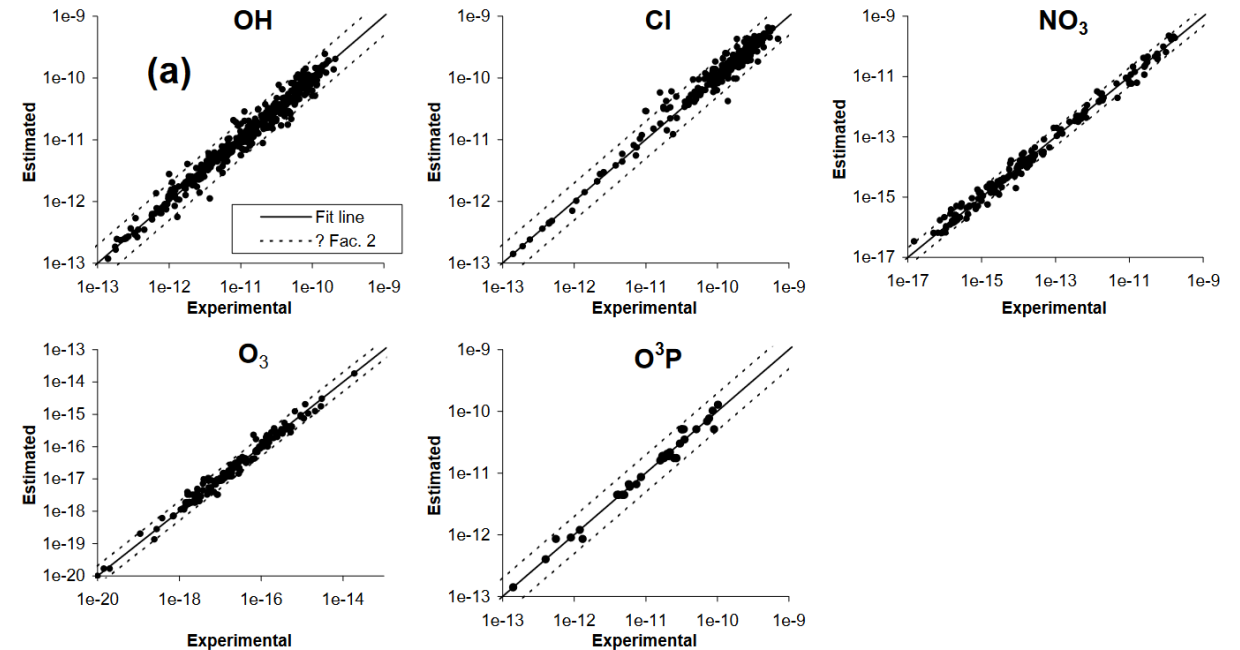
Example calculation from: Kwok and Atkinson (1995)

Structure-activity relationship principles

- Fundamentally, these are parameterizations, so, regardless of the approach, the idea is to describe the process of interest in a simplified way
- For SARs, this is linked to the molecular structure
- But the molecular property that is chosen for parameterization will change depending on the reaction mechanism
- For example, for the hydrogen abstraction reaction: $\text{RH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{R}$, a description of the strength of the R–H bond may be best
- On the other hand, for OH addition reactions:
 $\text{R}_1(\text{R}_2)\text{C}=\text{C}(\text{R}_3)\text{R}_4 + \text{OH} \rightarrow \text{R}_1(\text{R}_2)(\text{OH})\text{C}=\text{C}(\text{R}_3)\text{R}_4$, a description of the electron density of the C=C bond may be the best approach

Structure-activity relationship performance

- High quality measurements may determine k within $\sim 5\%$
- SARs tend to be accurate to within a factor of 2
- There is no replacement for high-quality laboratory data, but models need to contain reasonable information



Source: Carter (2020)

Databases to find kinetic data

NIST Chemical Kinetics Database:

<https://kinetics.nist.gov/kinetics/>

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation:

<https://iupac-aeris.ipsl.fr/>

NASA/ JPL data evaluation:

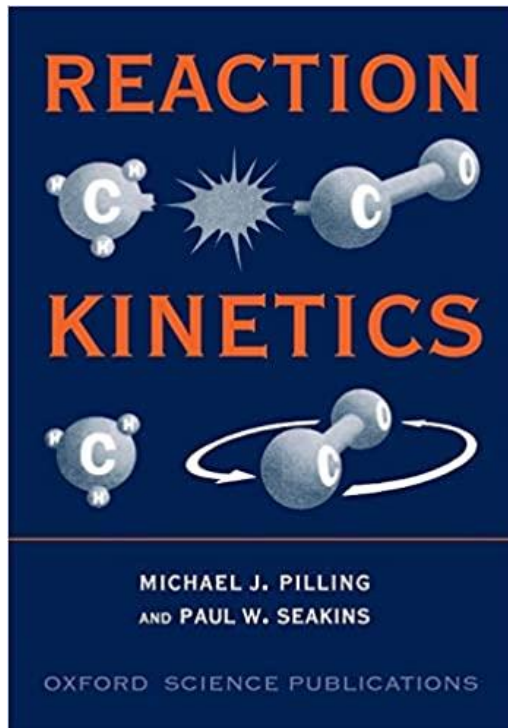
<https://jpldataeval.jpl.nasa.gov/>

Database for the kinetics of the gas-phase atmospheric reactions of organic compounds:

<https://data.eurochamp.org/data-access/kin/#/home>

Further reading

- This was a really quick introduction to the science of kinetics, if you would like to learn more about it, consider the following book:



Conclusions

- Kinetics has important effects in all aspects of atmospheric chemistry
- Kinetics is a fundamental quantity that can be measured with a variety of analytical and experimental techniques
- This quantity often varies according to the atmospheric conditions (temperature and pressure effects)
- Atmospheric chemistry produces a huge variety of chemical products
- This leads to an enormous parameter-space (too many to measure)
- So, we also need to think how we can estimate those things that we don't have time to measure