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Laboratory experiments for measuring kinetic parameters

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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

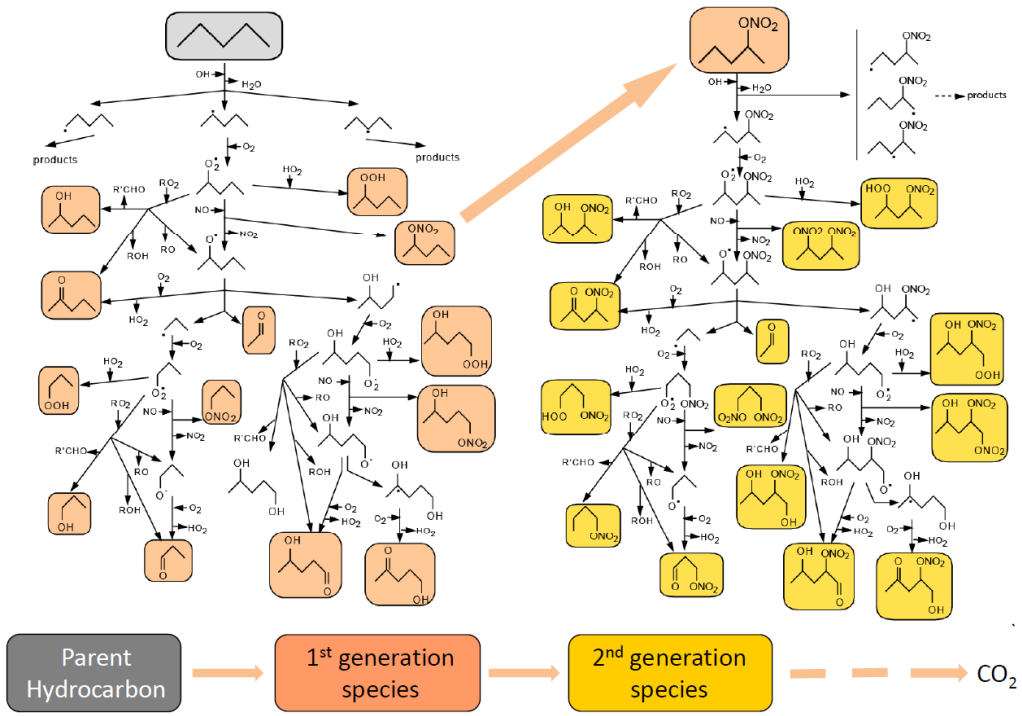
Kinetic parameters of the atmosphere

Carte du jour

- Photolysis:
  - $O_3 + h\nu \rightarrow O(^1D) + O_2$
- Thermal decomposition:
  - $CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO + NO_2$
- Radical–molecule:
  - OH + isoprene → products
- Radical–radical:
  - $RO_2 + RO_2 \rightarrow RO + RO + O_2$
- Termolecular reactions:
  - $OH + SO_2 + M \rightarrow \rightarrow H_2SO_4 + M$
- Equilibria:
  - $NO_2 + NO_3 \rightleftharpoons N_2O_5$
- Phase transfer:
  - Gas-phase → 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

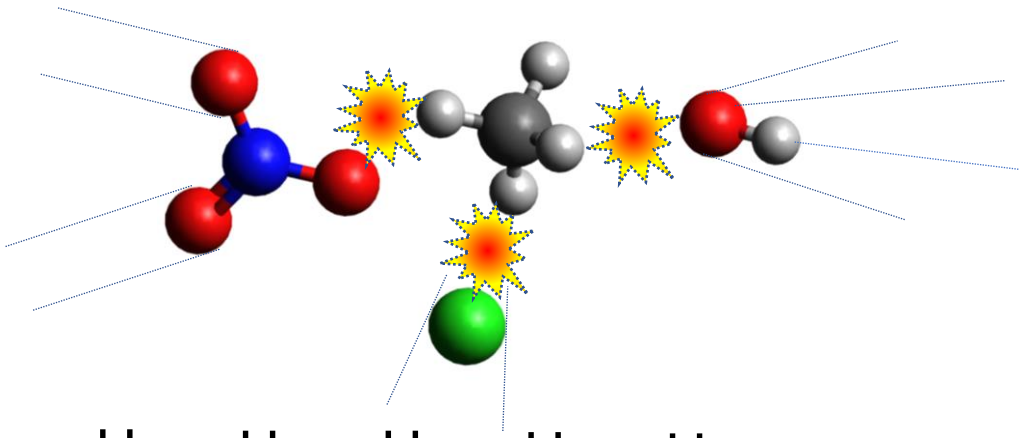


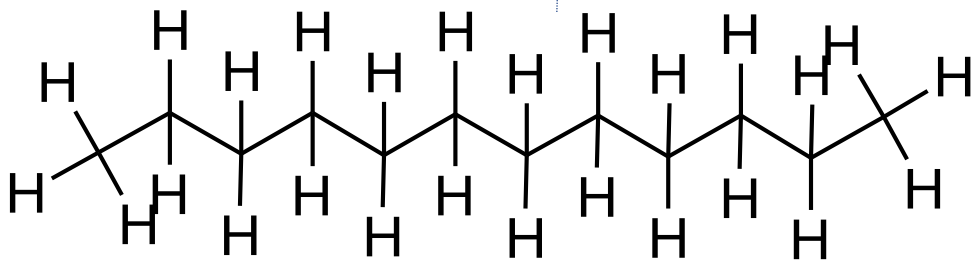
Types of competition

- 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?





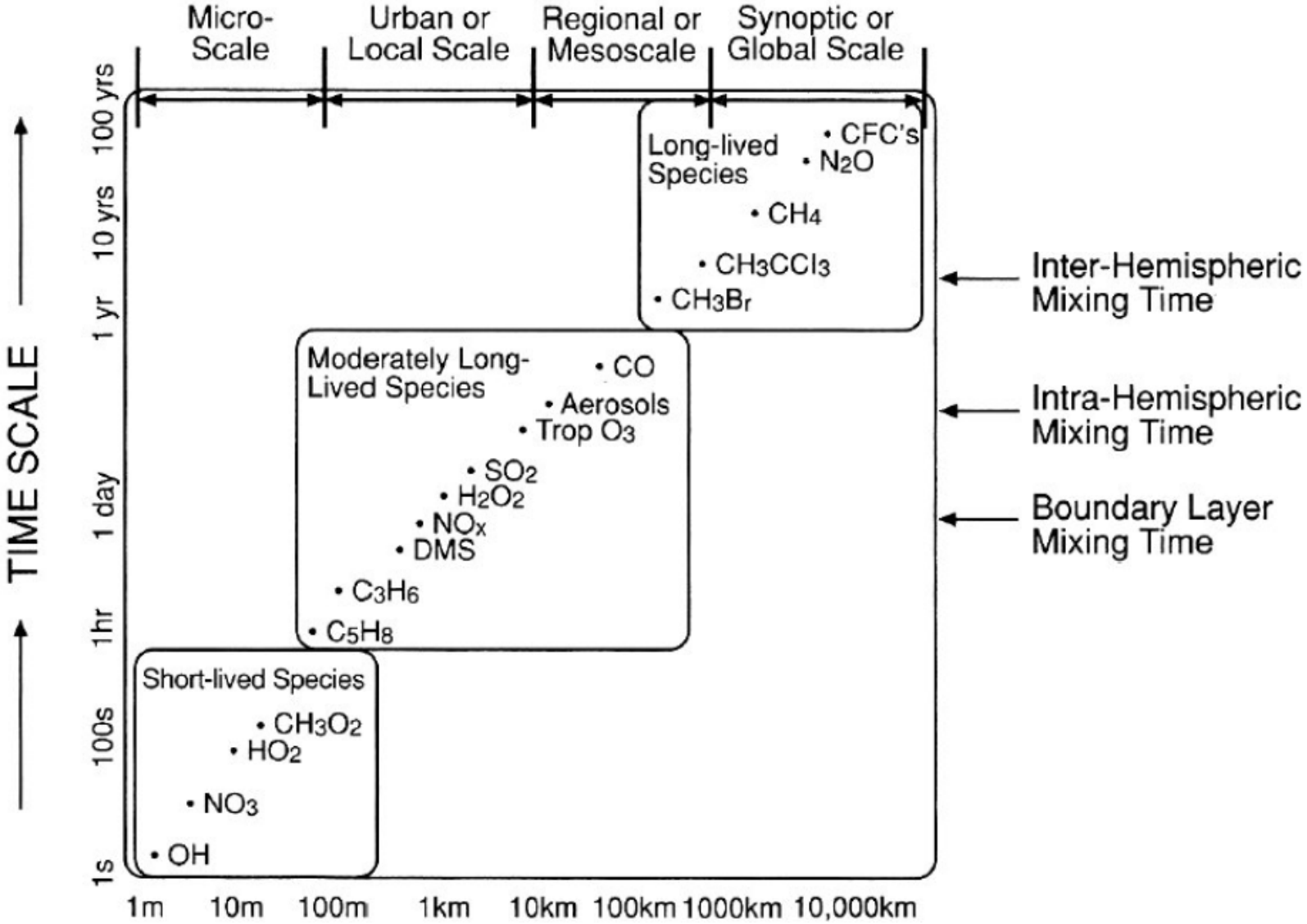
$RO_2 + RO_2 \rightarrow RO + RO + O_2$

$\mathbf{R}O_2 + \mathbf{R}O_2 \rightarrow \mathbf{R}OO\mathbf{R}$

Atmospheric lifetime

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

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



Why is the lifetime so important?

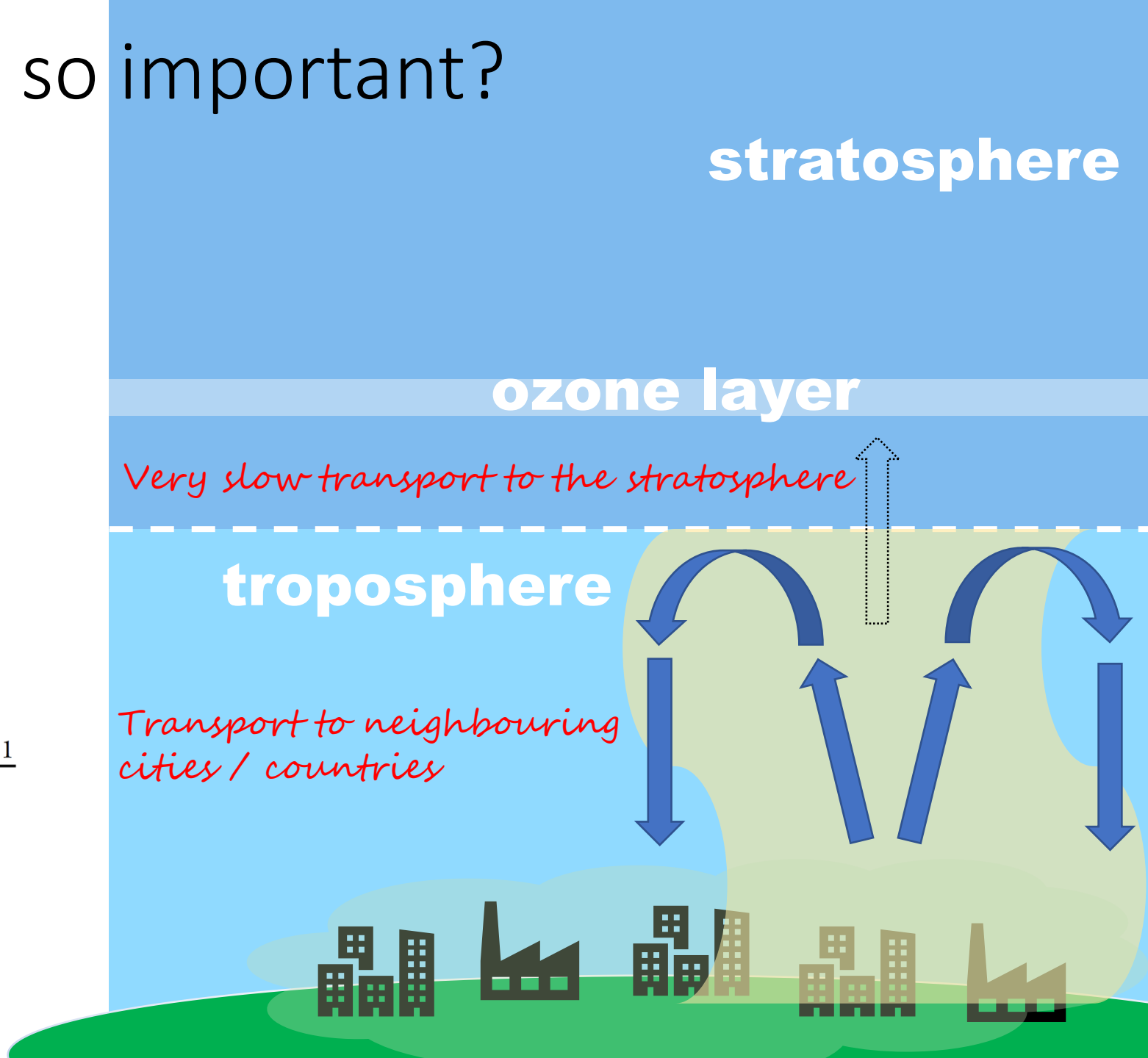
- Lifetime is a major control on the distance over which pollution can be transported
- The pollution from one country could affect the air quality of another
- Furthermore, for certain chemicals, vertical transport (and persistence) becomes important (e.g. CFCs, HCFCs)

For example:

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

For example:

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



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:

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

- 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*)

$$\tau = \frac{1}{k[\mathrm{OH}]} \qquad \tau_{\mathrm{O_3}} = \frac{1}{k[\mathrm{O_3}]}$$

etcetera …

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

similarly … $\tau_{\mathrm{photolysis}} = \frac{1}{J}$

The rate coefficient, *k*

- Simple atmospheric chemical reactions are first-order, A ⟶ 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 ⟶ 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 N_2 at room temperature:

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

- 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. ≈ 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 emparts a temperature dependence:

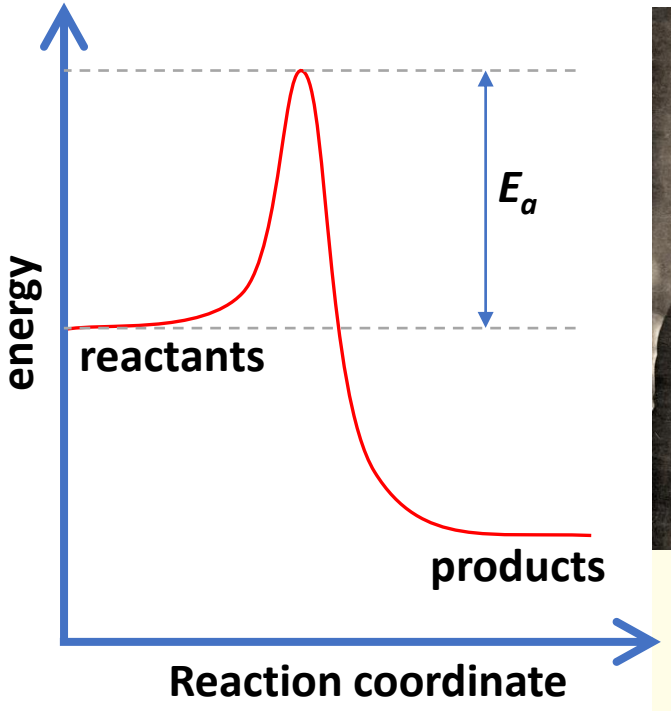
$k(T) = Z\exp(-E_a/\mathrm{RT})$

- Other (steric) factors are also important:

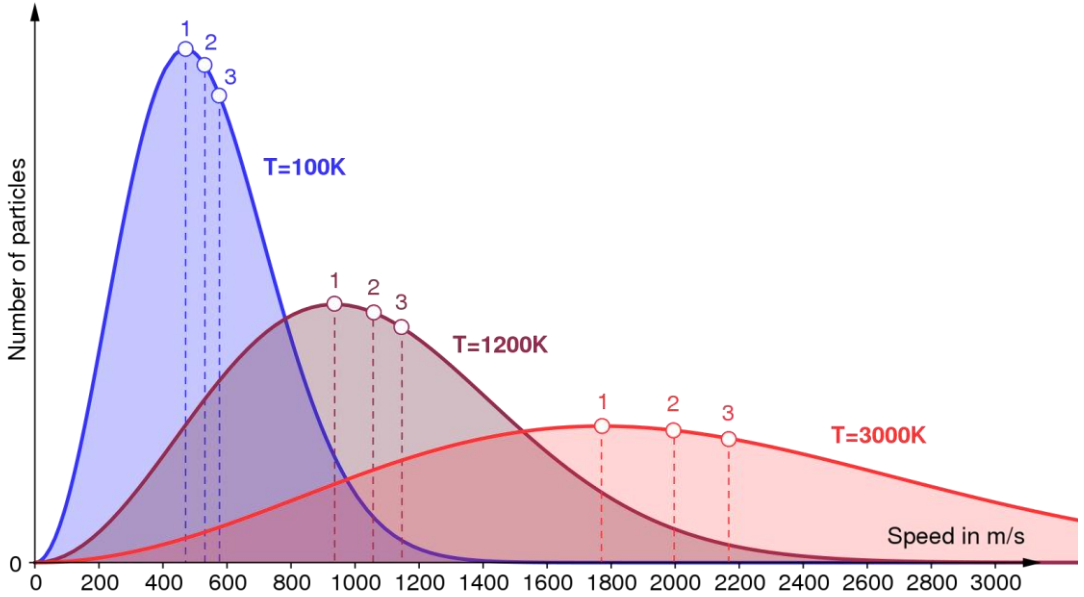
$k(T) = Z\rho\exp(-E_a/\mathrm{RT})$

- Leading to the familiar Arrhenius equation:

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



Svante Arrhenius (1889)



How do we measure kinetic parameters?

Let's consider a bi-molecular reaction (A + B ⟶ 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

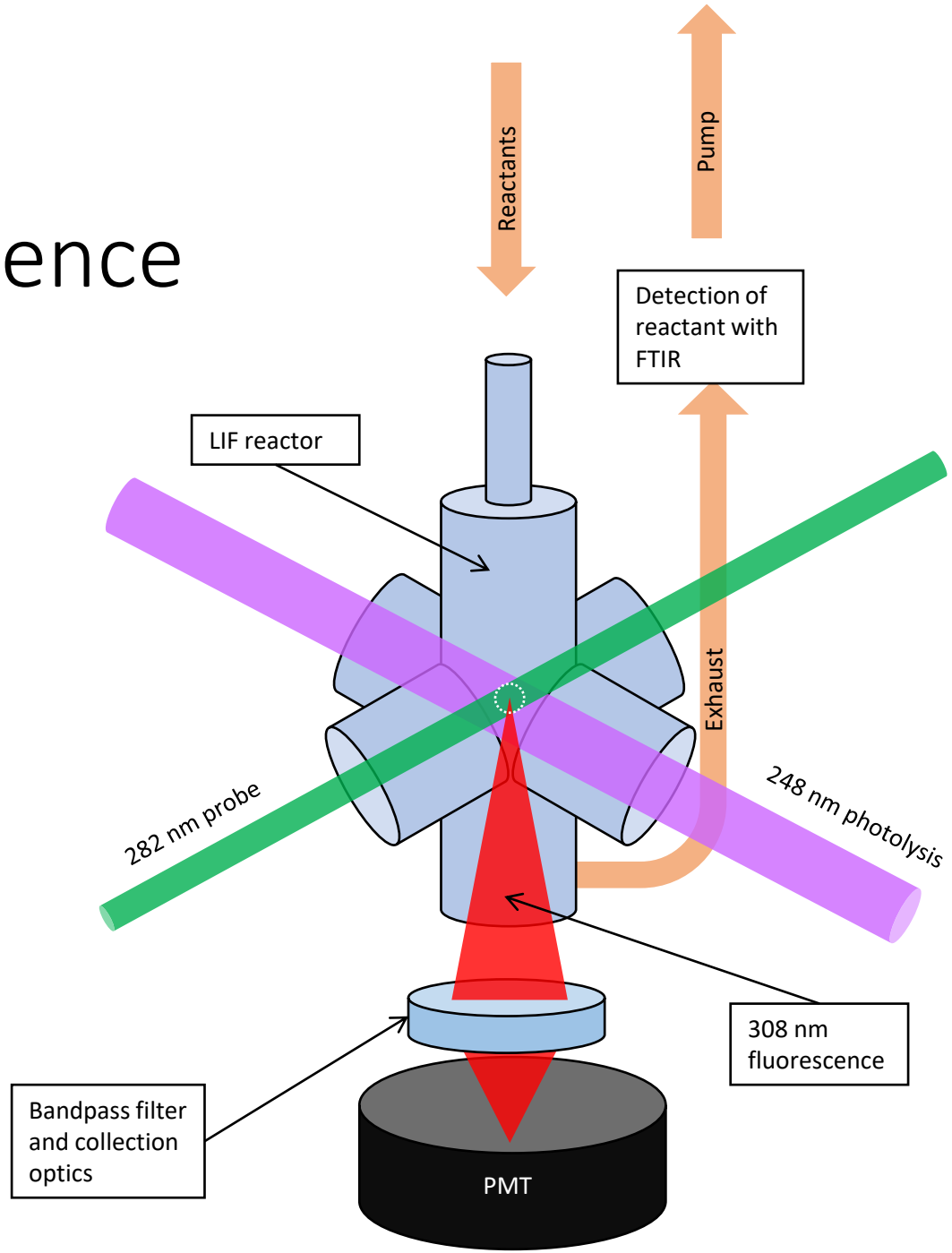
B. An analytical tool to measure (at least one of) A, B or C
   - Needs to be sensitive enough, and rapid enough

$$-\frac{d[A]}{dt} = k_{obs}[A]$$

C. A measurement of time
   - A way of exposing A to B for a known amount of time

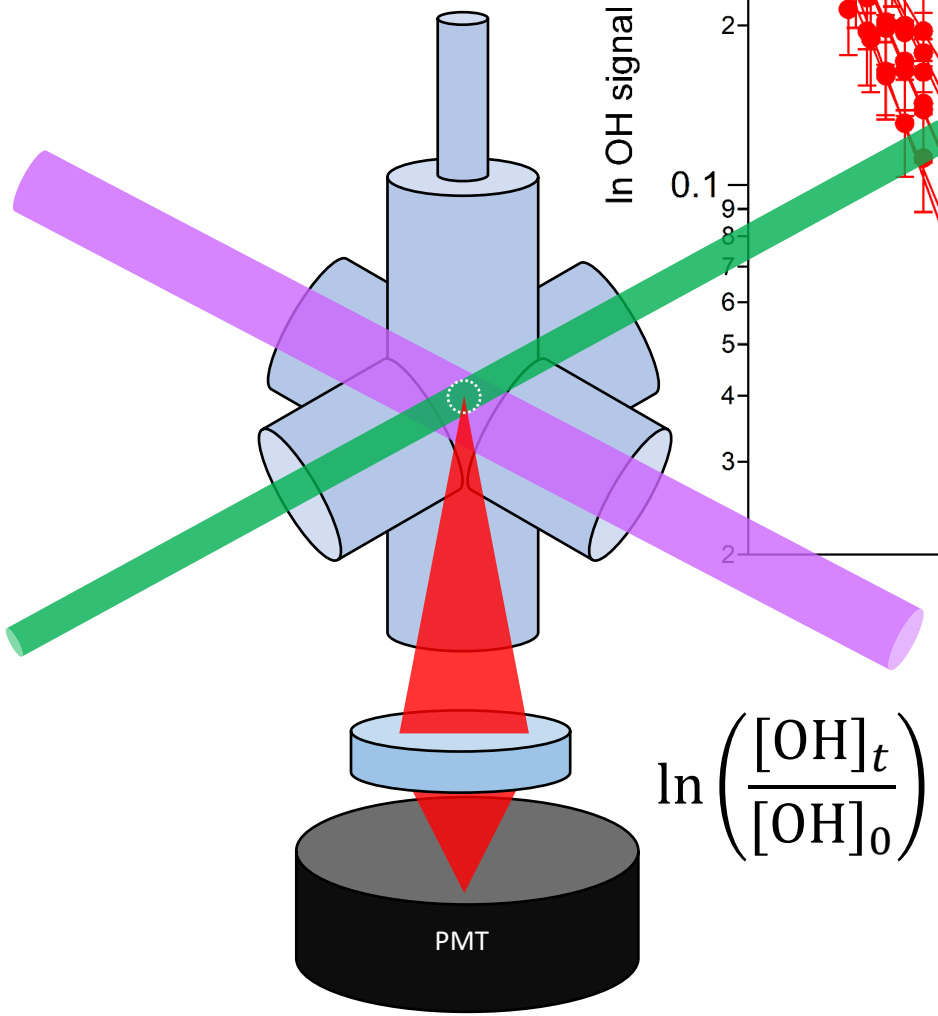
$$-\frac{d[A]}{dt} = k_{obs}[A]$$

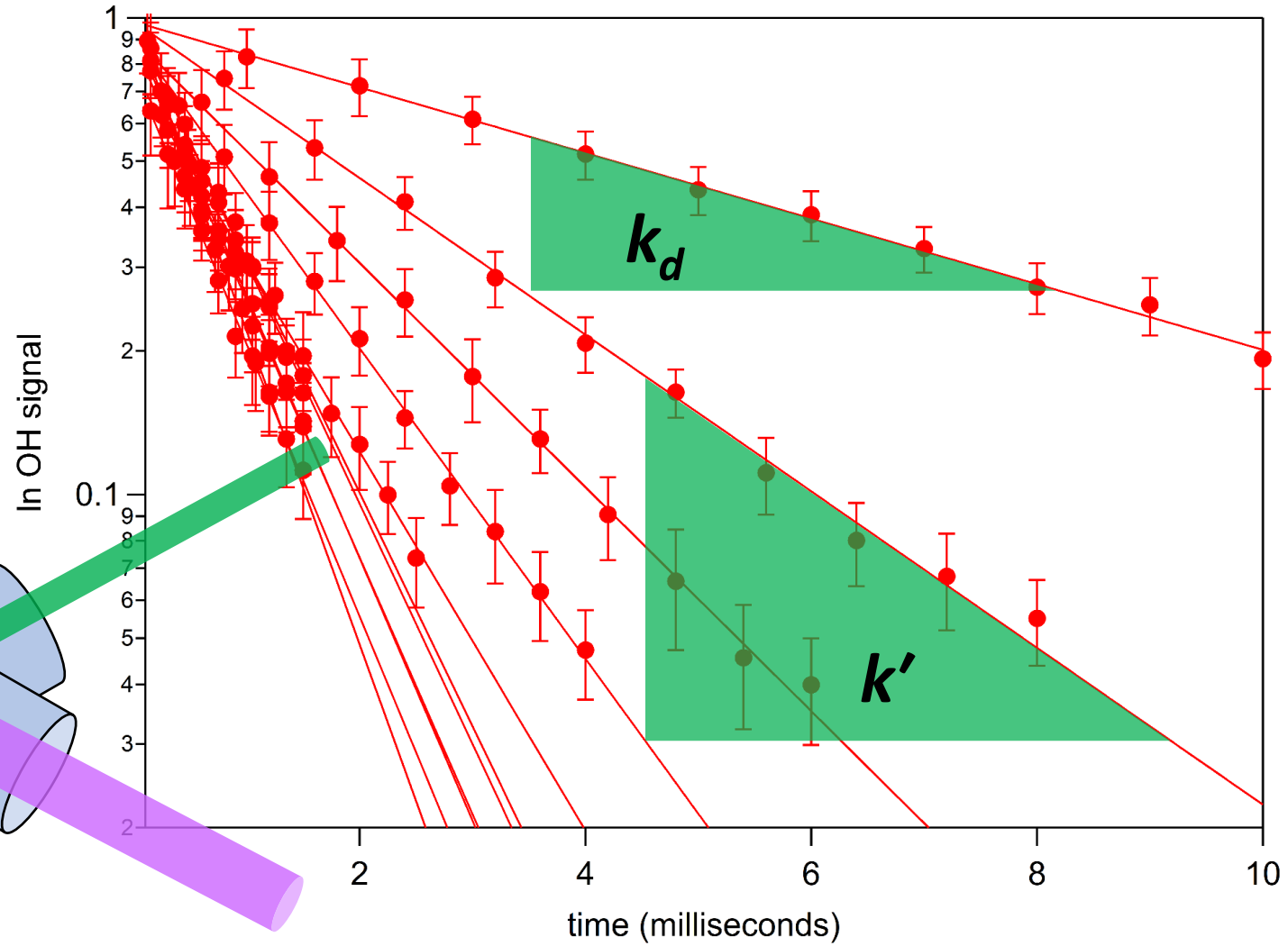
Laser Induced Fluorescence



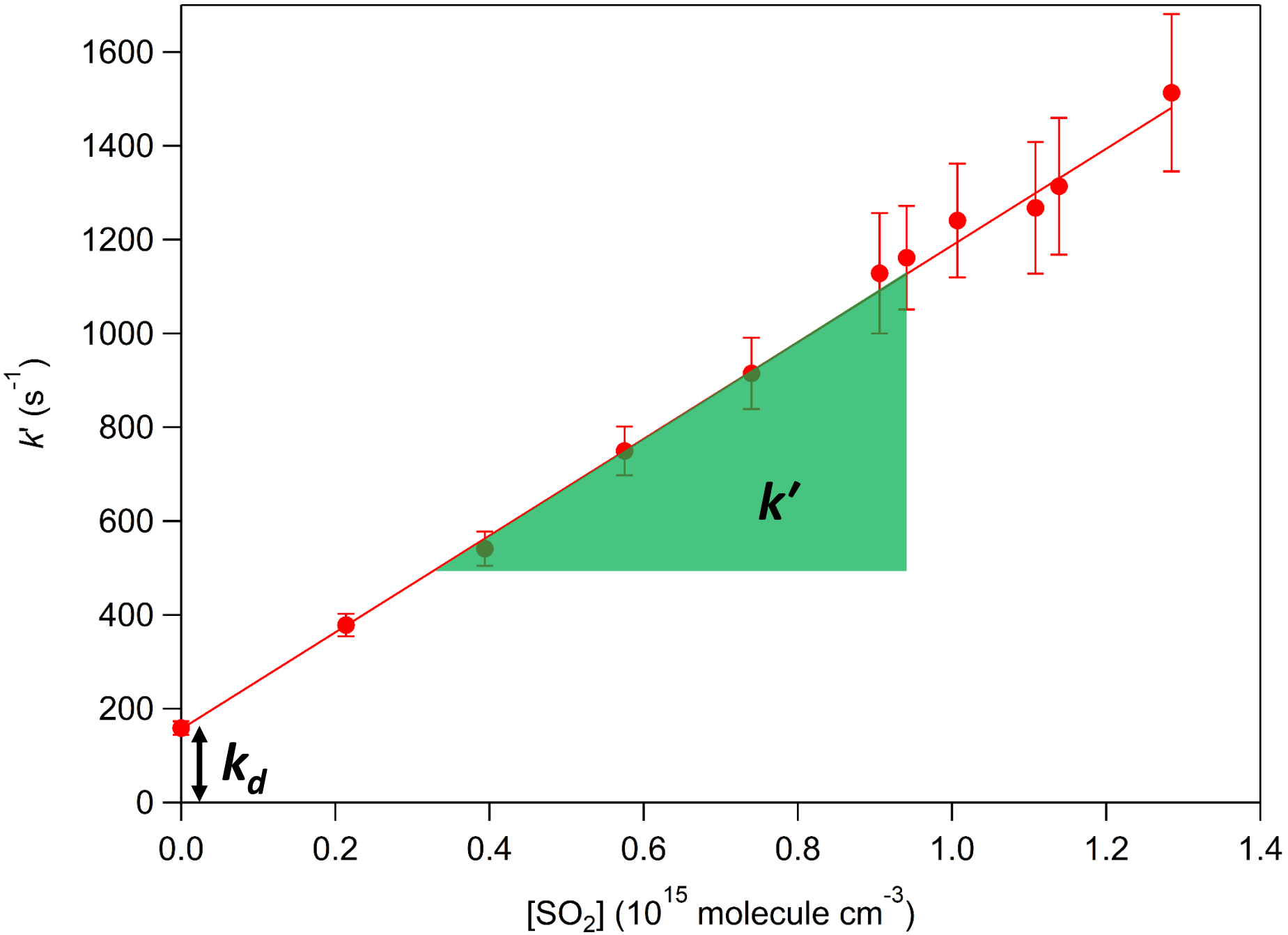
- Temperature range: 220–373 K
- Pressure range: 30–600 Torr
- Bath gases: He, Ar, N_2, O_2
- OH precursors: H_2O_2, HNO_3
- On-line measurement of $[SO_2]$
- Supporting RR measurements (N_2, Ar, O_2, Air)

Laser Induced Fluorescence

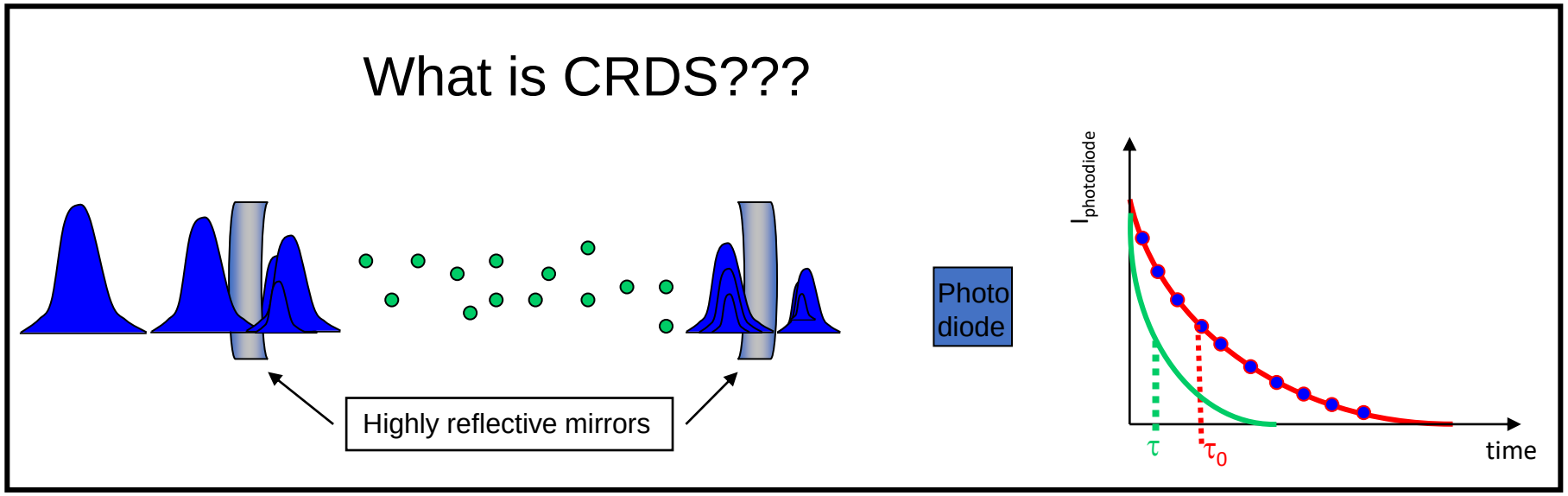




$$\ln\left(\frac{[\mathrm{OH}]_t}{[\mathrm{OH}]_0}\right) = \ln\left(\frac{S_t}{S_0}\right) = -(k[\mathrm{reactant}] + k_d)t = -k't$$


1600
1400
1200
1000
800
600
400
200
0
k′ (s-1)
k′
kd
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
[SO2] (1015 molecule cm-3)

Laser photolysis coupled to CRDS



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

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

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

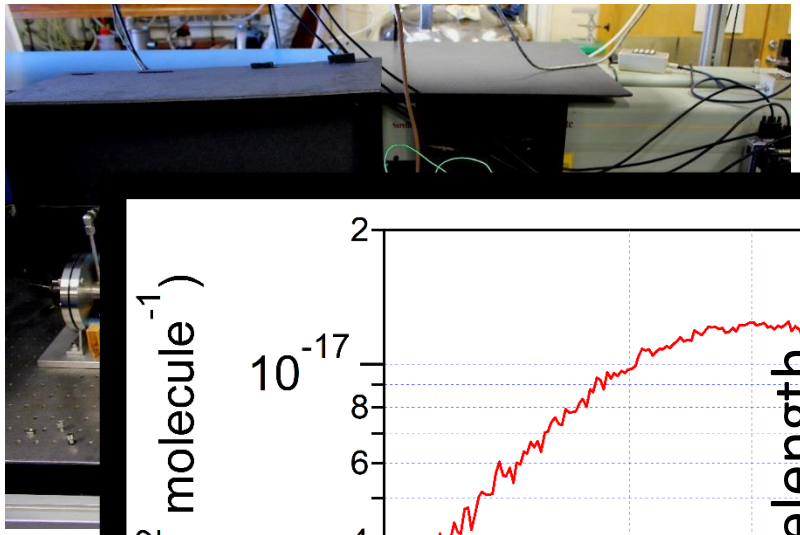
Convenient chemistry

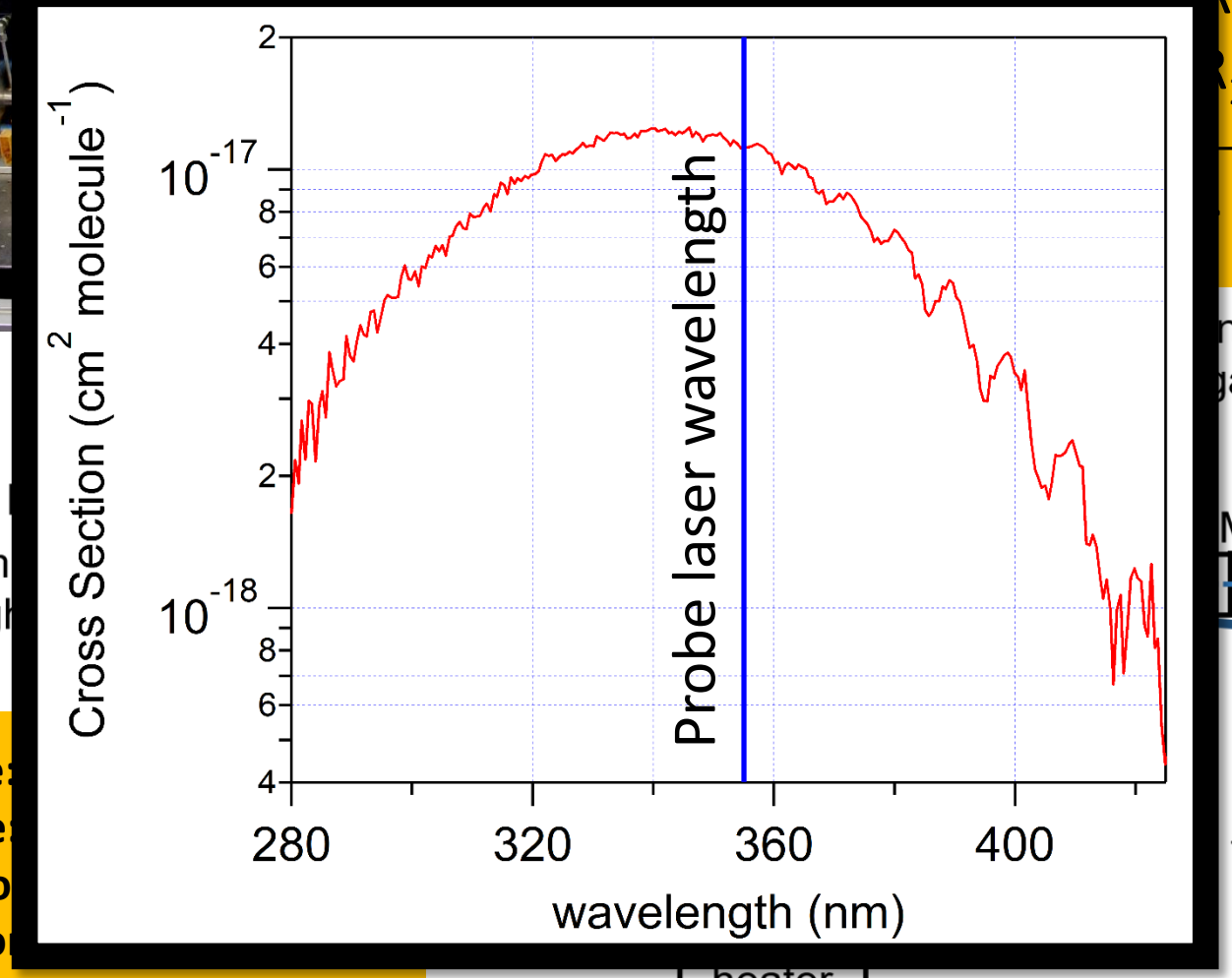
$R_2I + I$

$R_2OO + I$

$\rightarrow ICR_2OO + M$

CH_3





nd
gas

355 nm
probe ligh

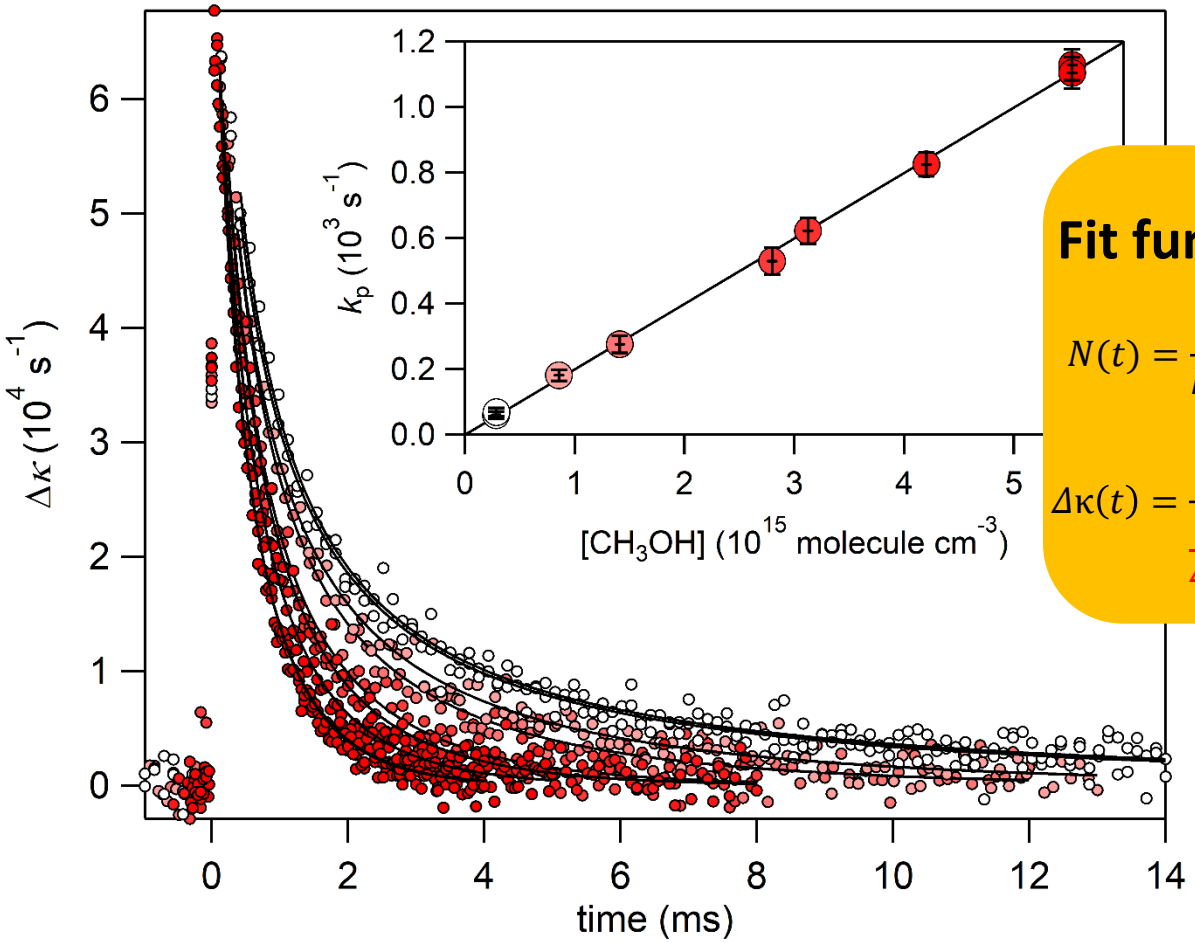
M

detector

mirror with N_2 purge
thermocouple
pressure gauge

heater

T range:
P range:
Ring-do
Reactio
$[Cl]_0$: ~2 × 10^{12} (molec. cm^{-3})

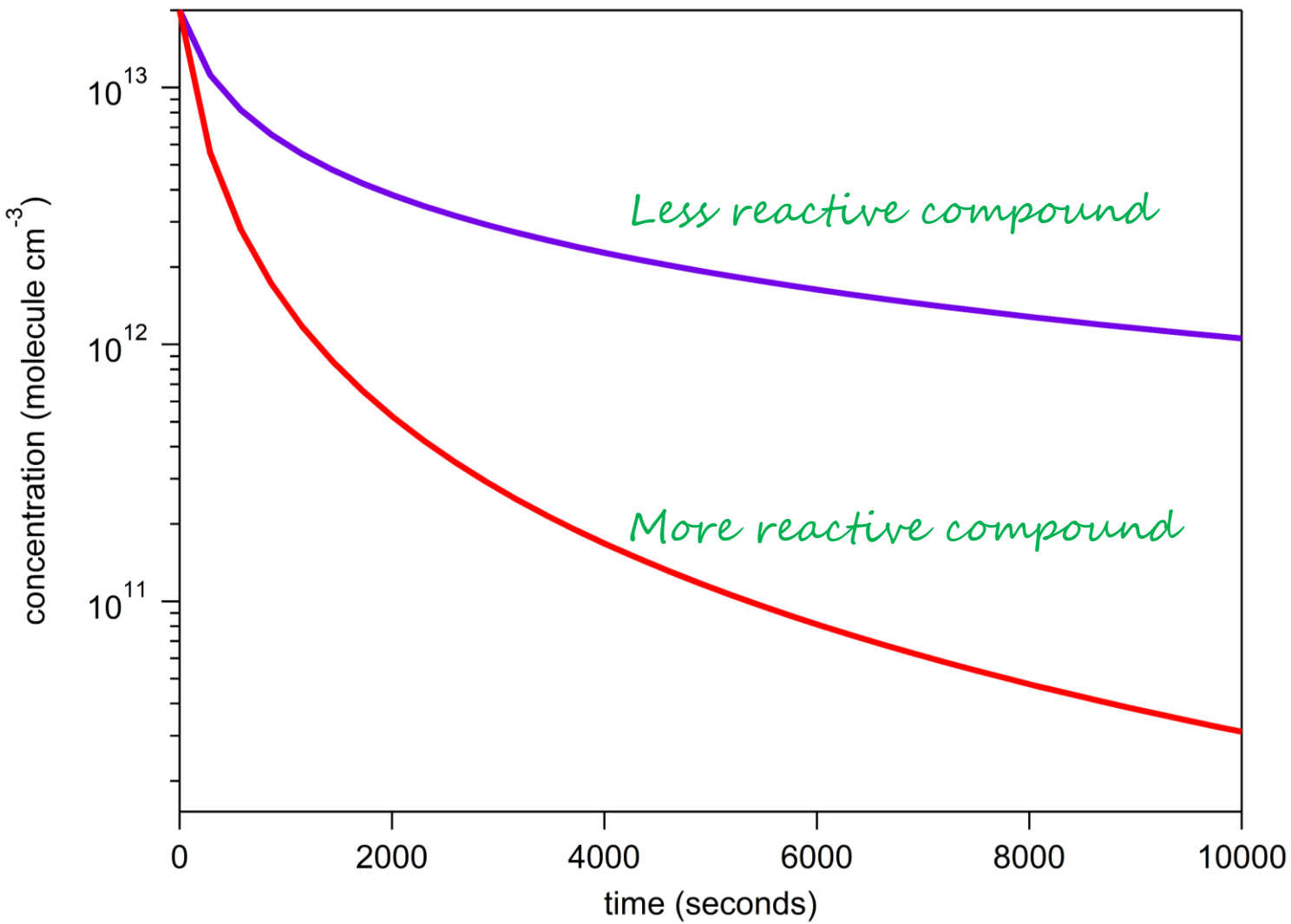


Fit function: $\frac{dN}{dt} = -2k_{obs}N^2 - k_pN$

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

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

Relative rate kinetics

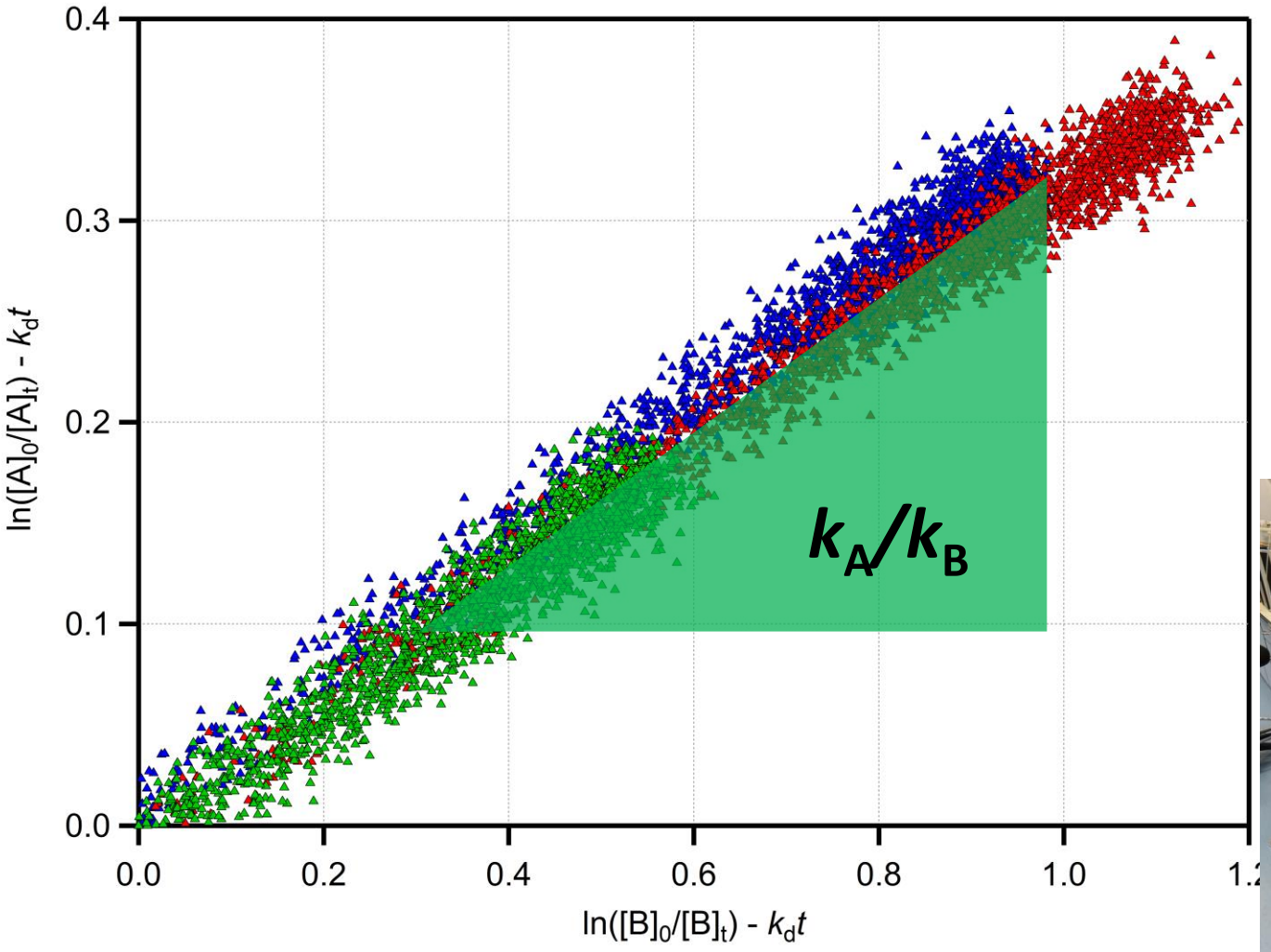


- Another approach is to use the relative rate approach
- Here we introduce two compounds that are allowed to react simultaneously:

  $A + OH \longrightarrow$ product

  $B + OH \longrightarrow$ product
- So, if we know the reactivity of B (for example), then we can deduce that of A

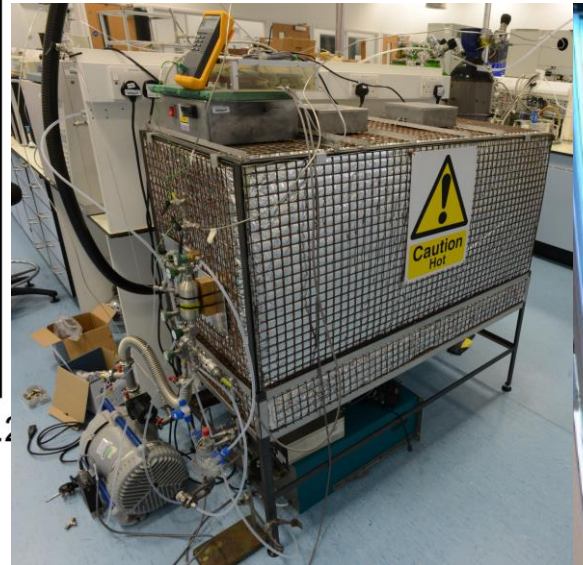
Relative rate kinetics



- This is done with the relative rate approach:

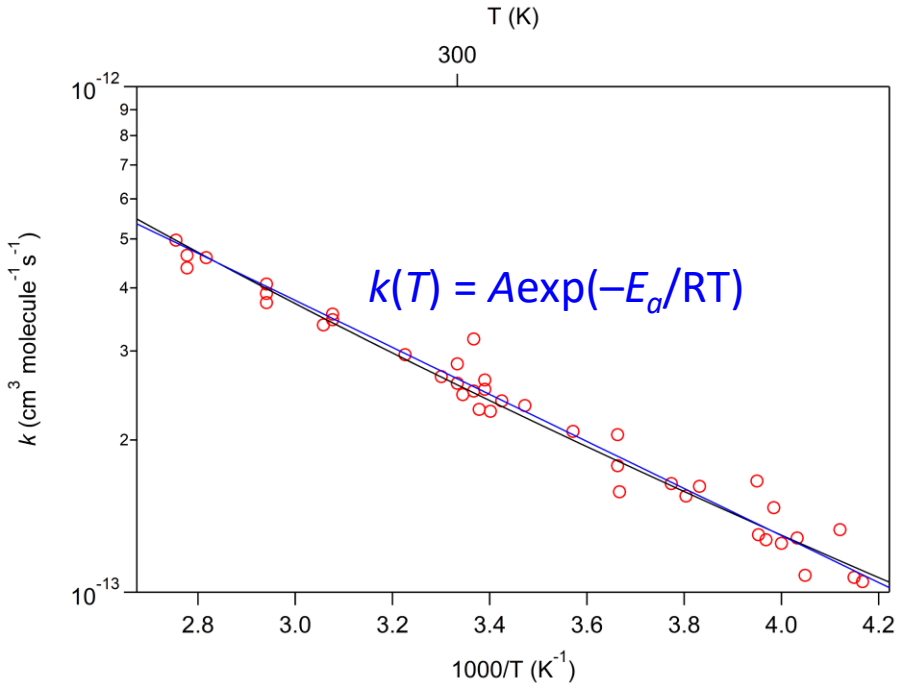
$$ln\left(\frac{[A]_0}{[A]_t}\right) - k_d t = \frac{k_A}{k_B} ln\left(\frac{B_0}{B_t}\right) - k_d t$$

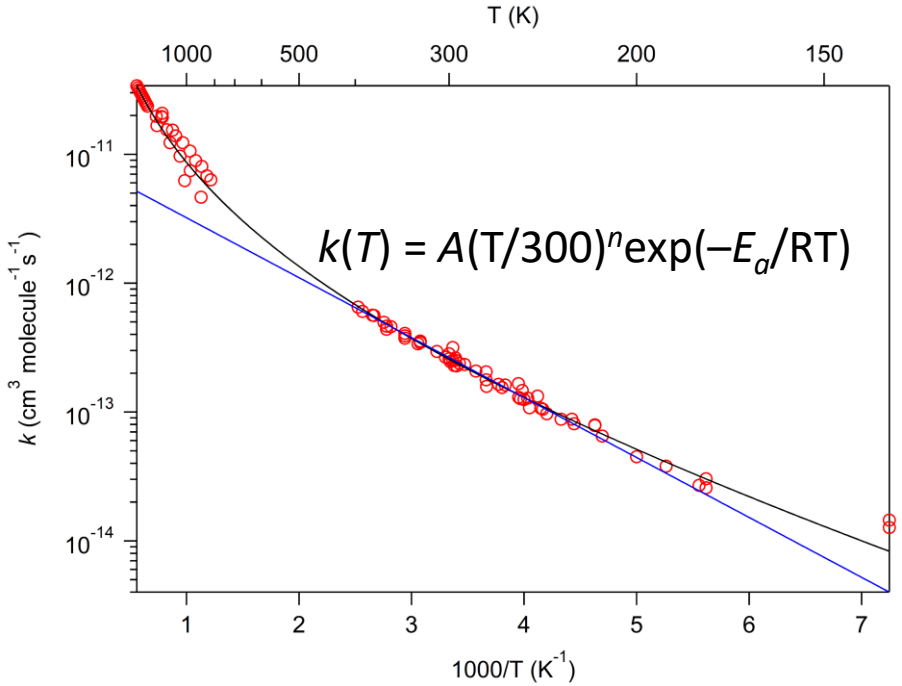
- This can be very precise and effective, but it is limited by the accuracy of the reference



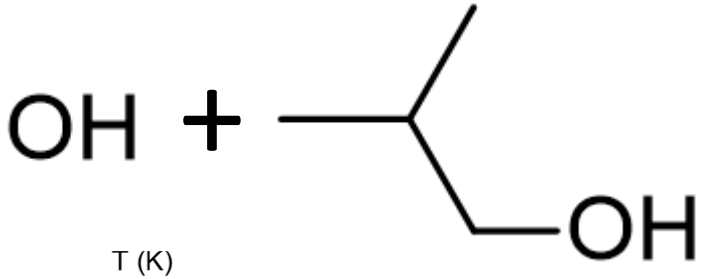
T-dependence of *k*

- 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



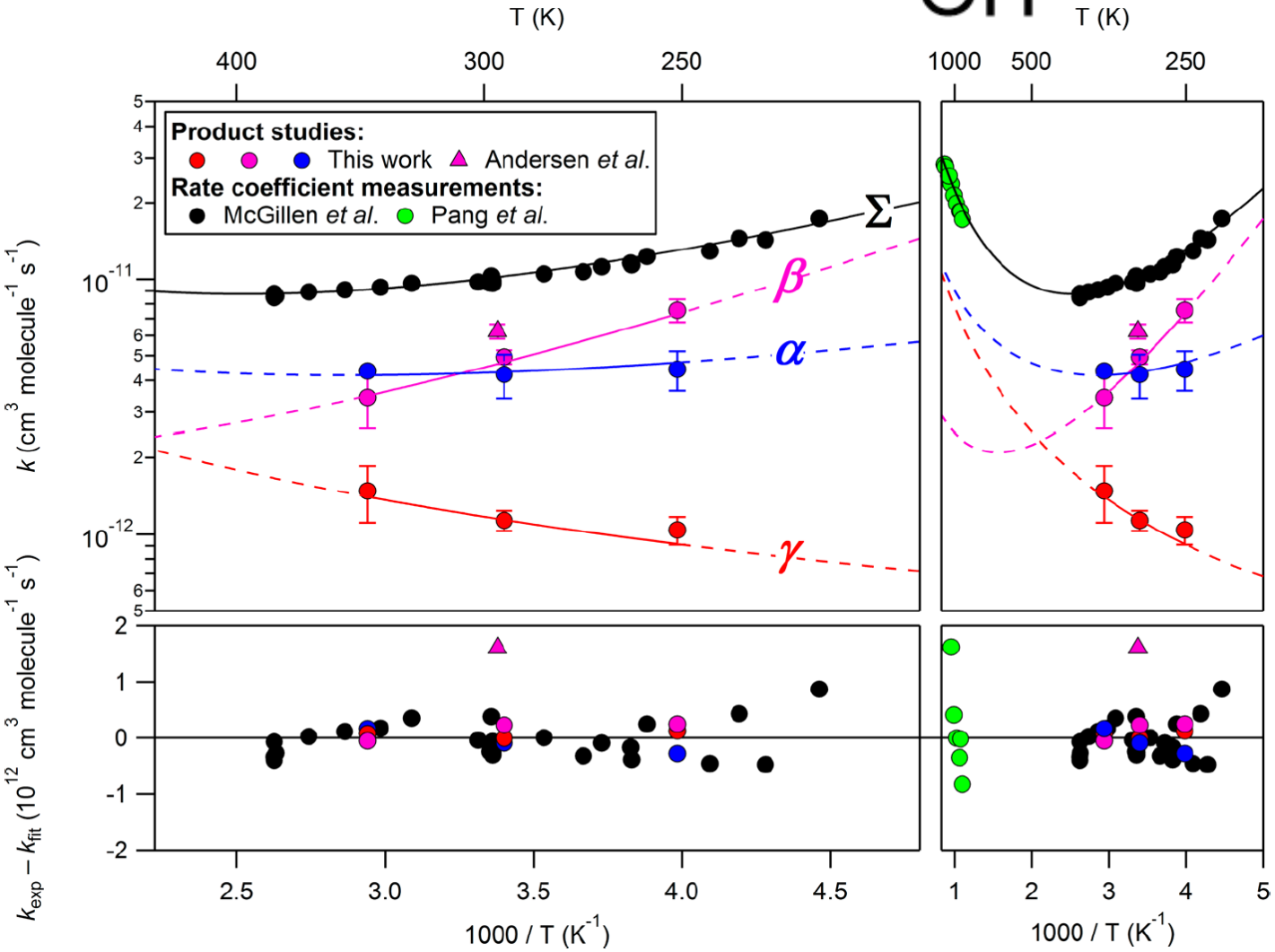


Non-Arrhenius behaviour



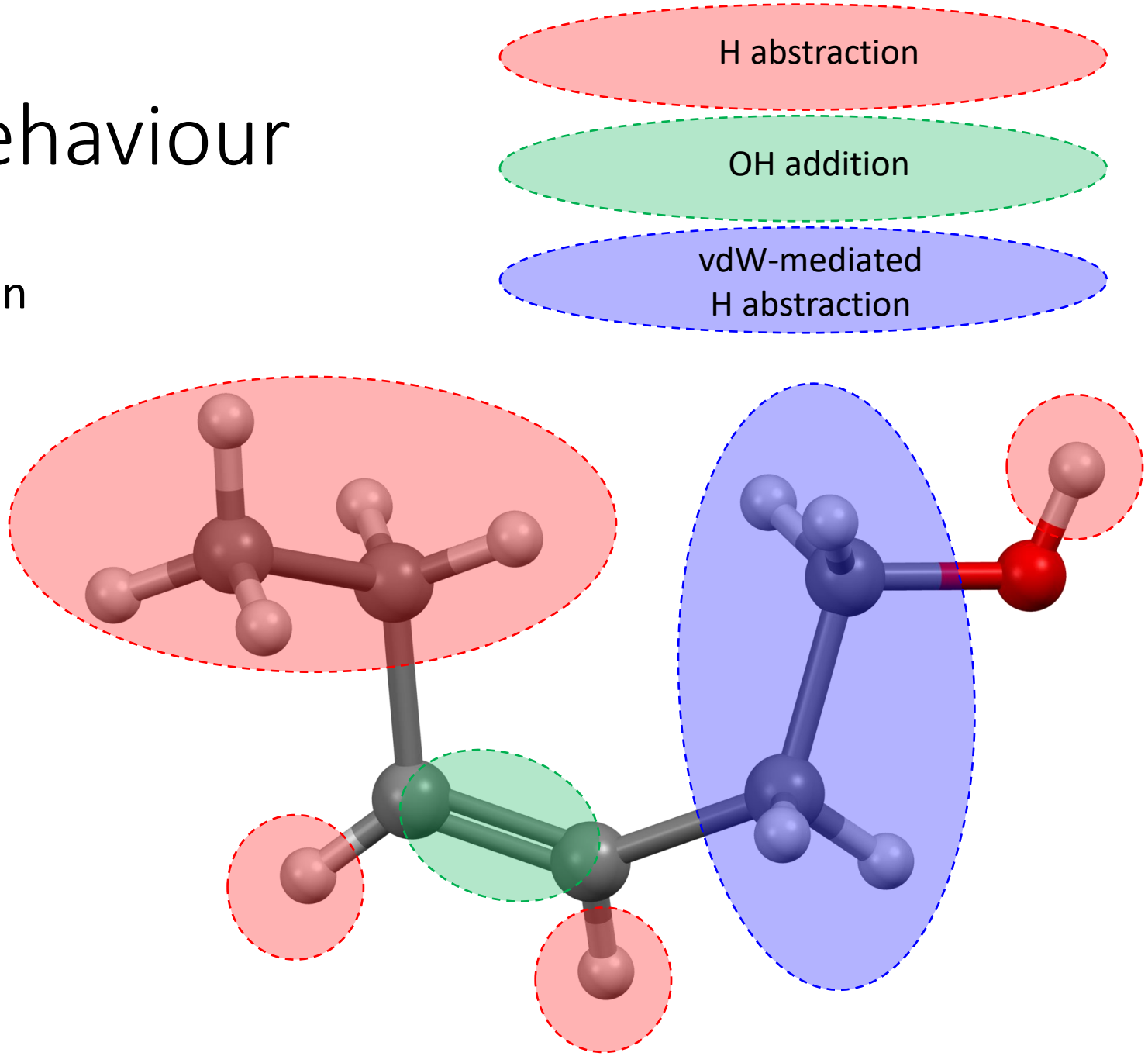
- Several reasons for this:
- Multiple (*i*) reactions sites, each with their own different T-dependence
- Since the total reaction rate is the sum of each:

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



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?



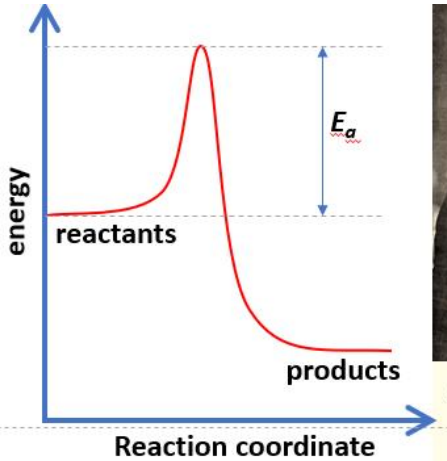
Negative temperature-dependence of *k*

- 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:

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



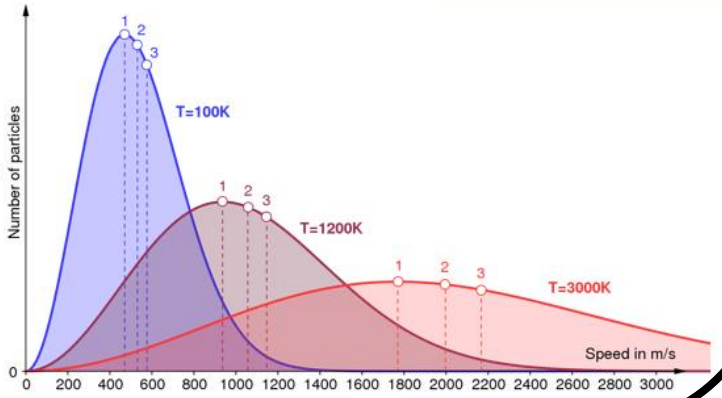
Svante Arrhenius (1889)

- Other (steric) factors are also important:

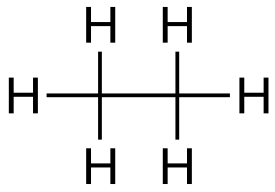
$k(T) = Z\rho\exp(-E_a/RT)$

- Leading to the familiar Arrhenius equation:

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

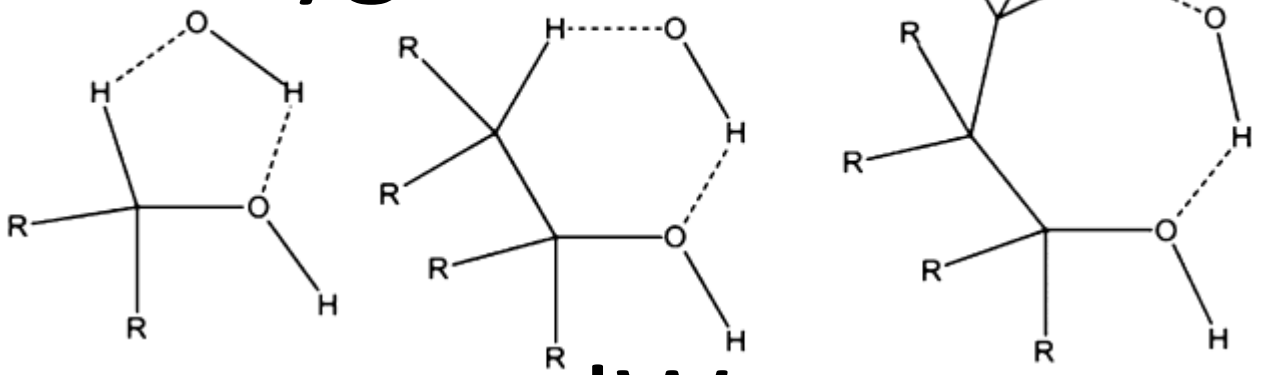


OH +

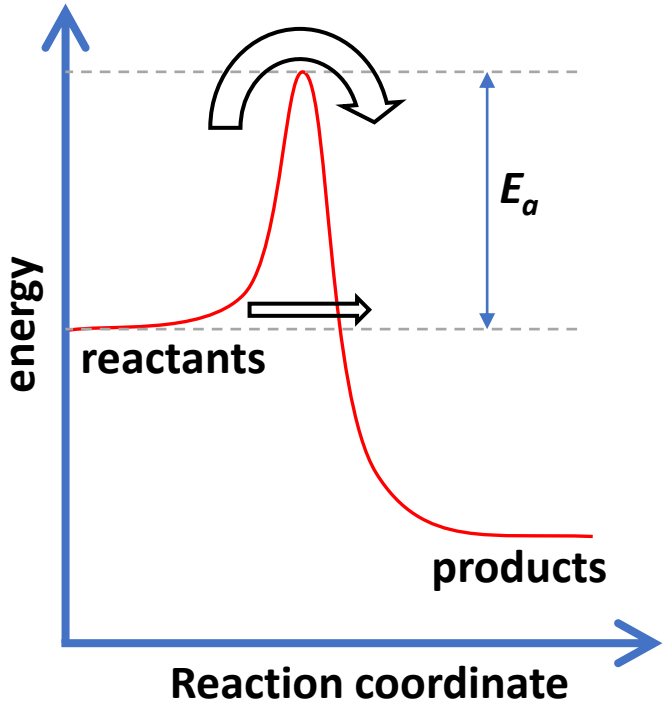


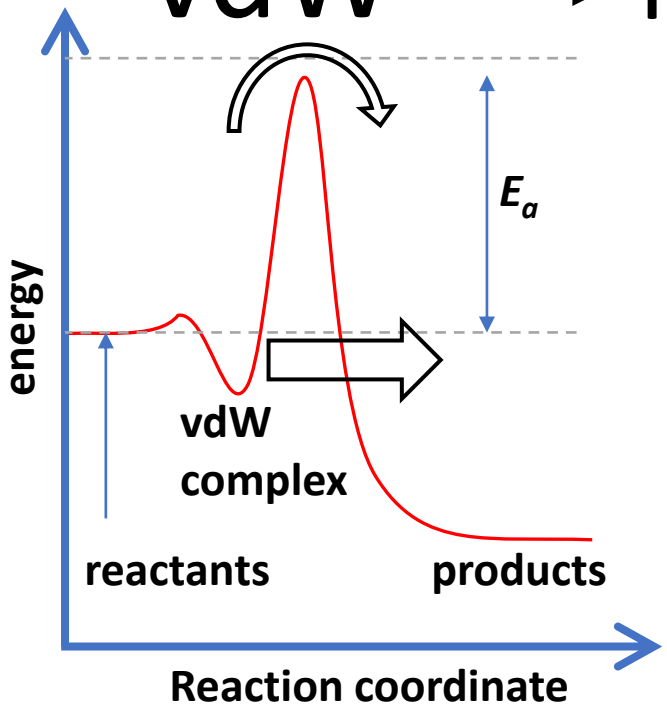
→ R· + H_2O

OH + oxygenate



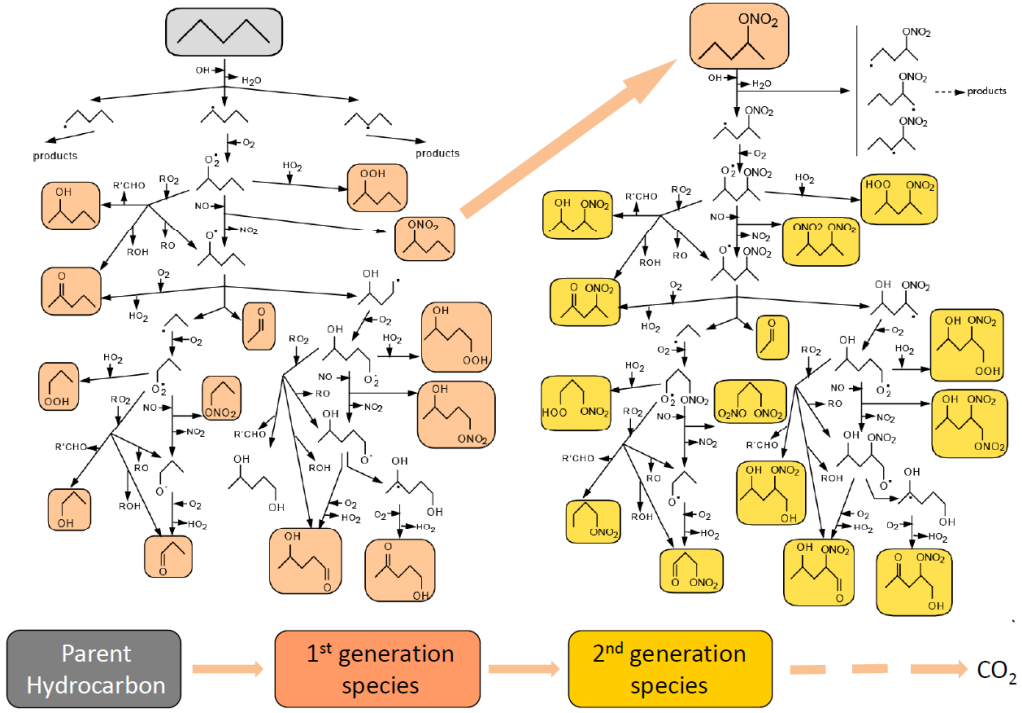
vdW → R· + H_2O





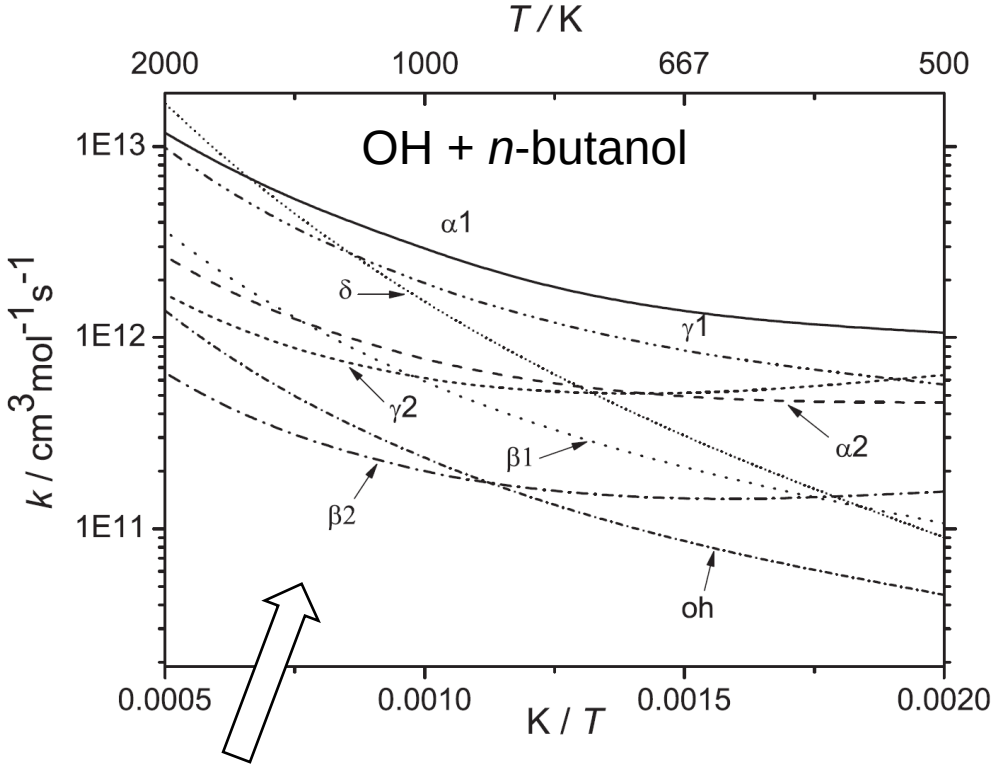
Negative temperature-dependence of *k*

- 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

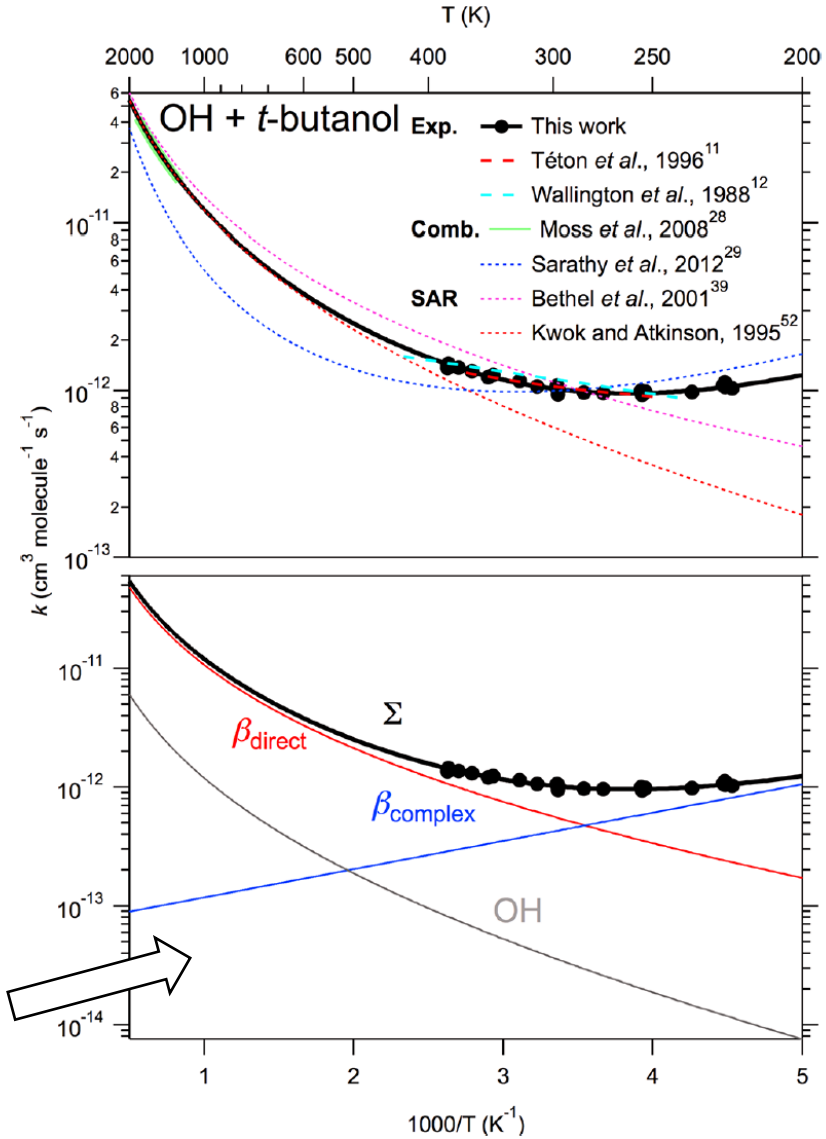


Almost all atmospheric degradation products are oxygenated

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

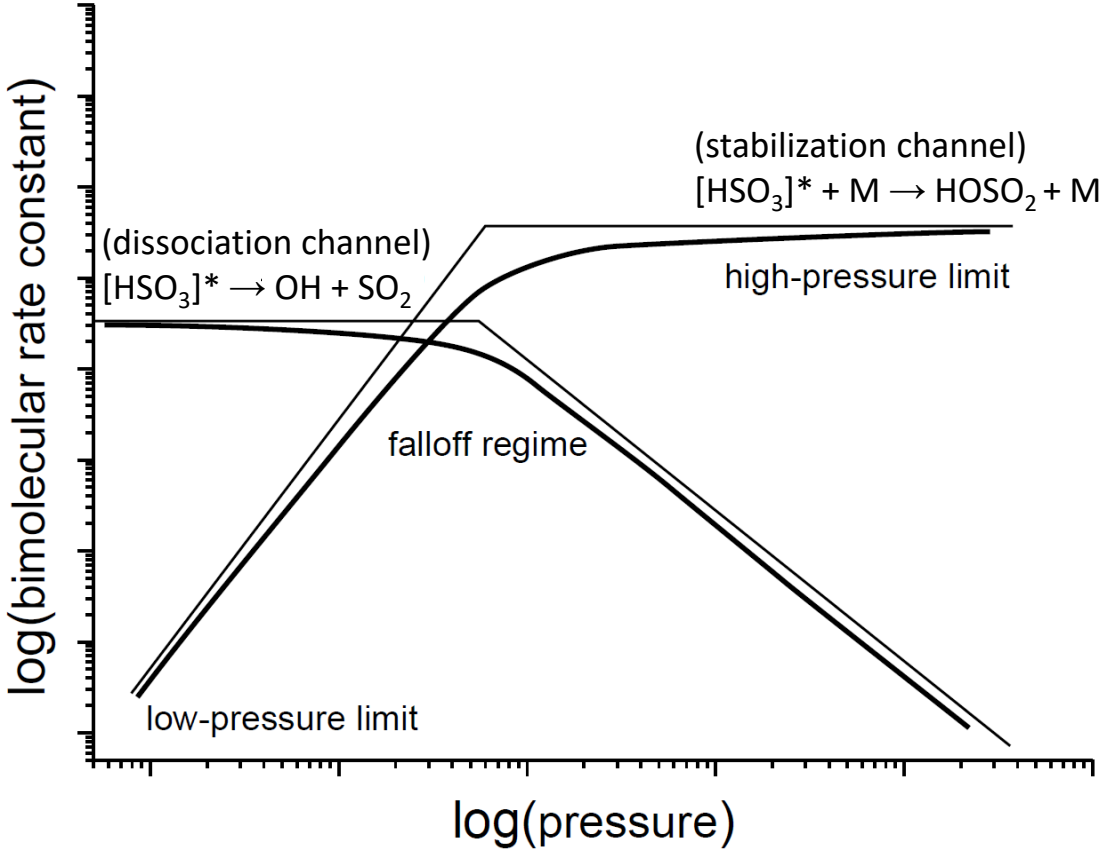
Pressure-dependence of *k*

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

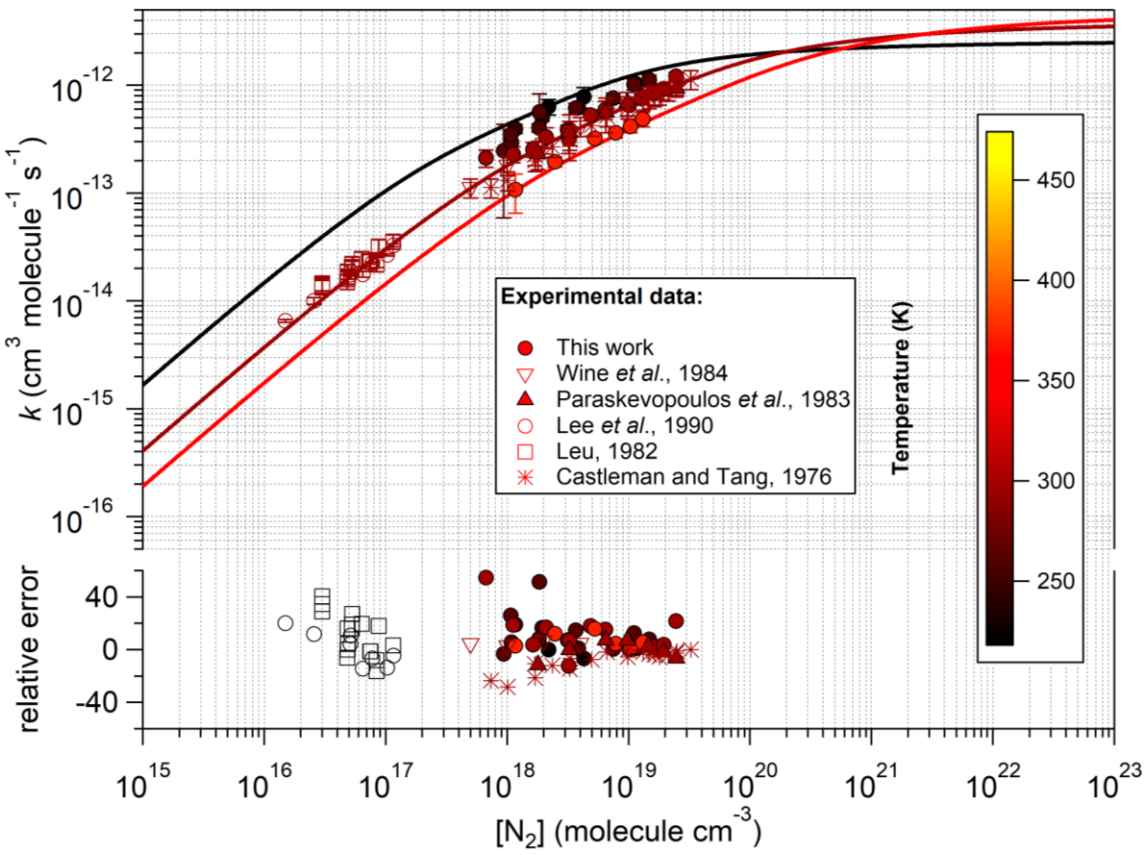
- This is a competition: can $[HOSO_2]^*$ collide with M before it falls apart?
- Therefore, this reaction dependends on [M] ($\propto$ pressure)

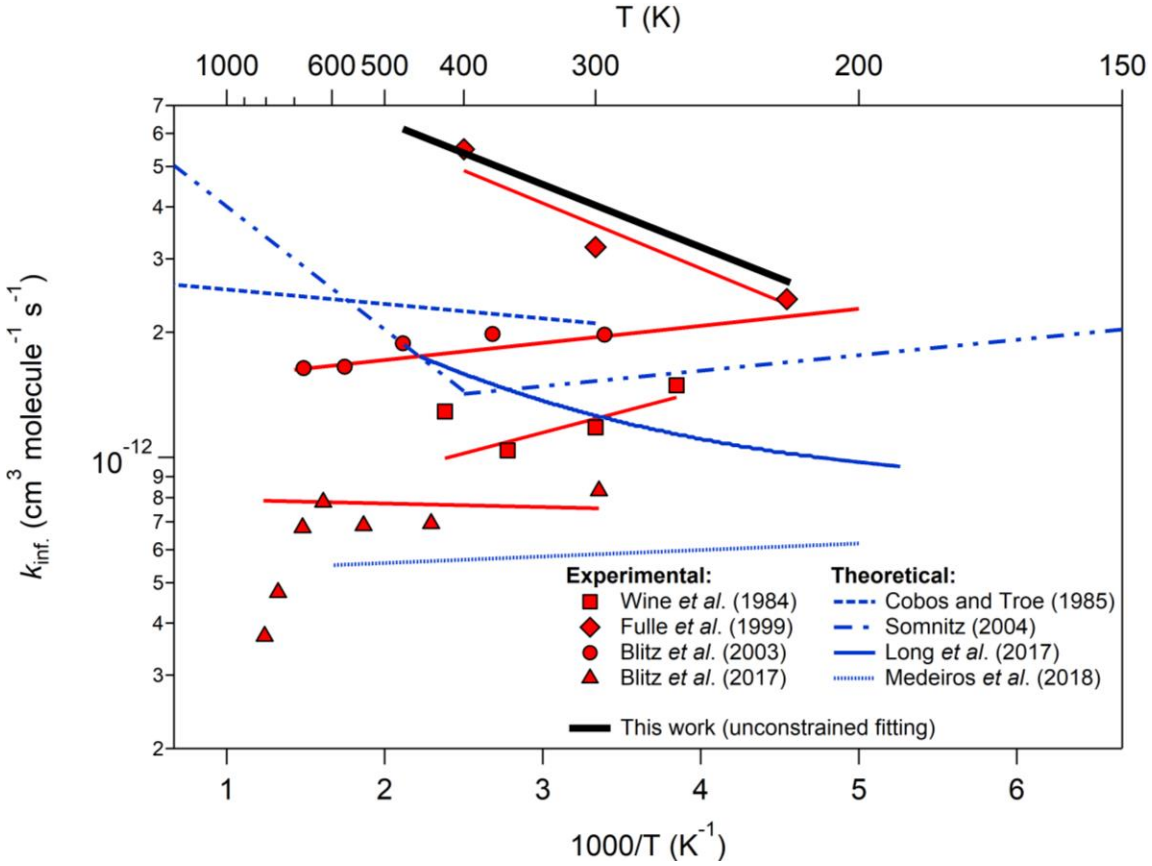
kinetics in the fall-off regime



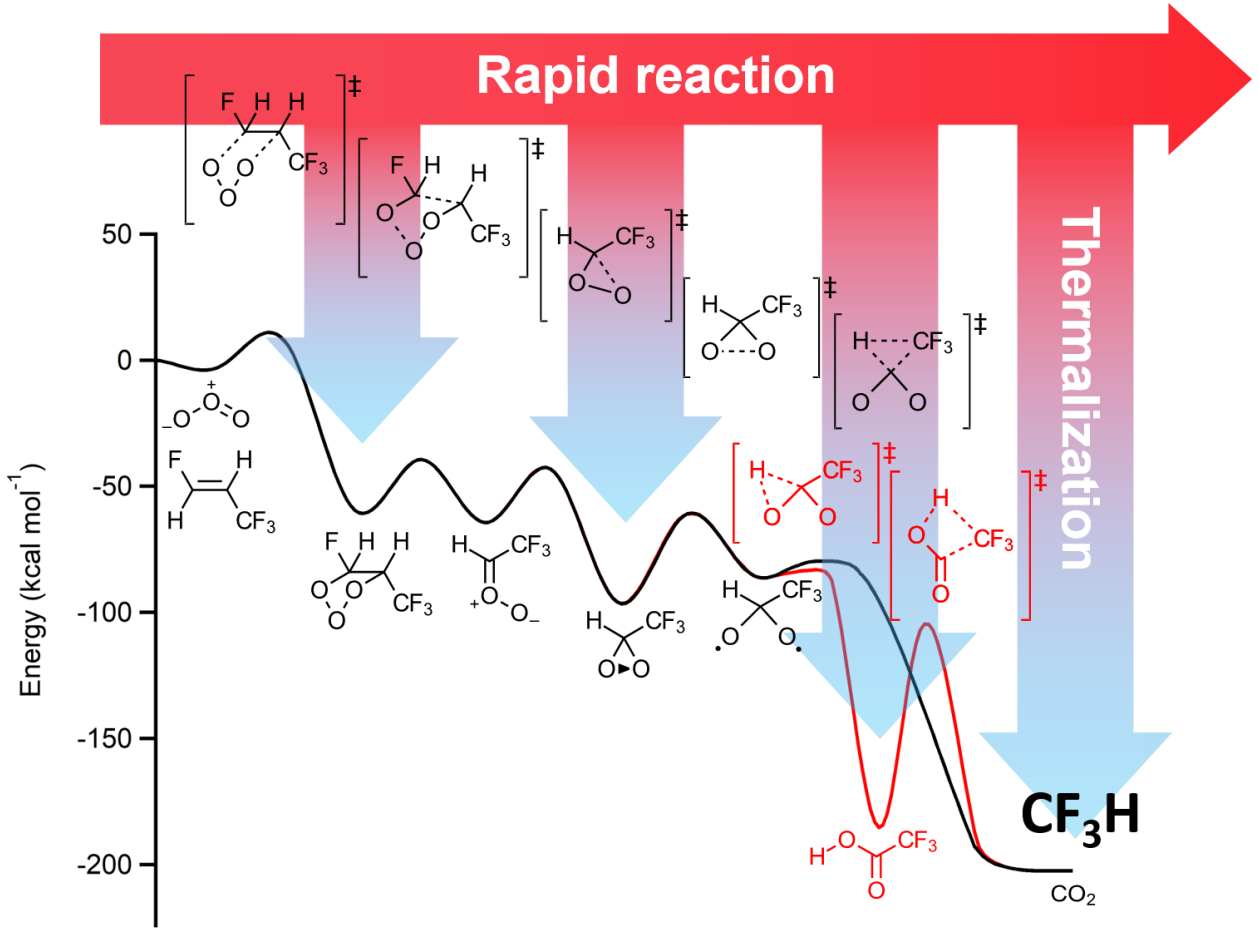
- Where atmospheric pressure dependence is important, reactions are usually in the fall-off region
- At some point, *k* cannot get any larger, it has reached its high-pressure limit (k_∞)
- The onset of k_∞ can vary widely <mBar – 100s of Bar
- This depends of the stability of the intermediate

P- and T-dependence in OH + SO_2





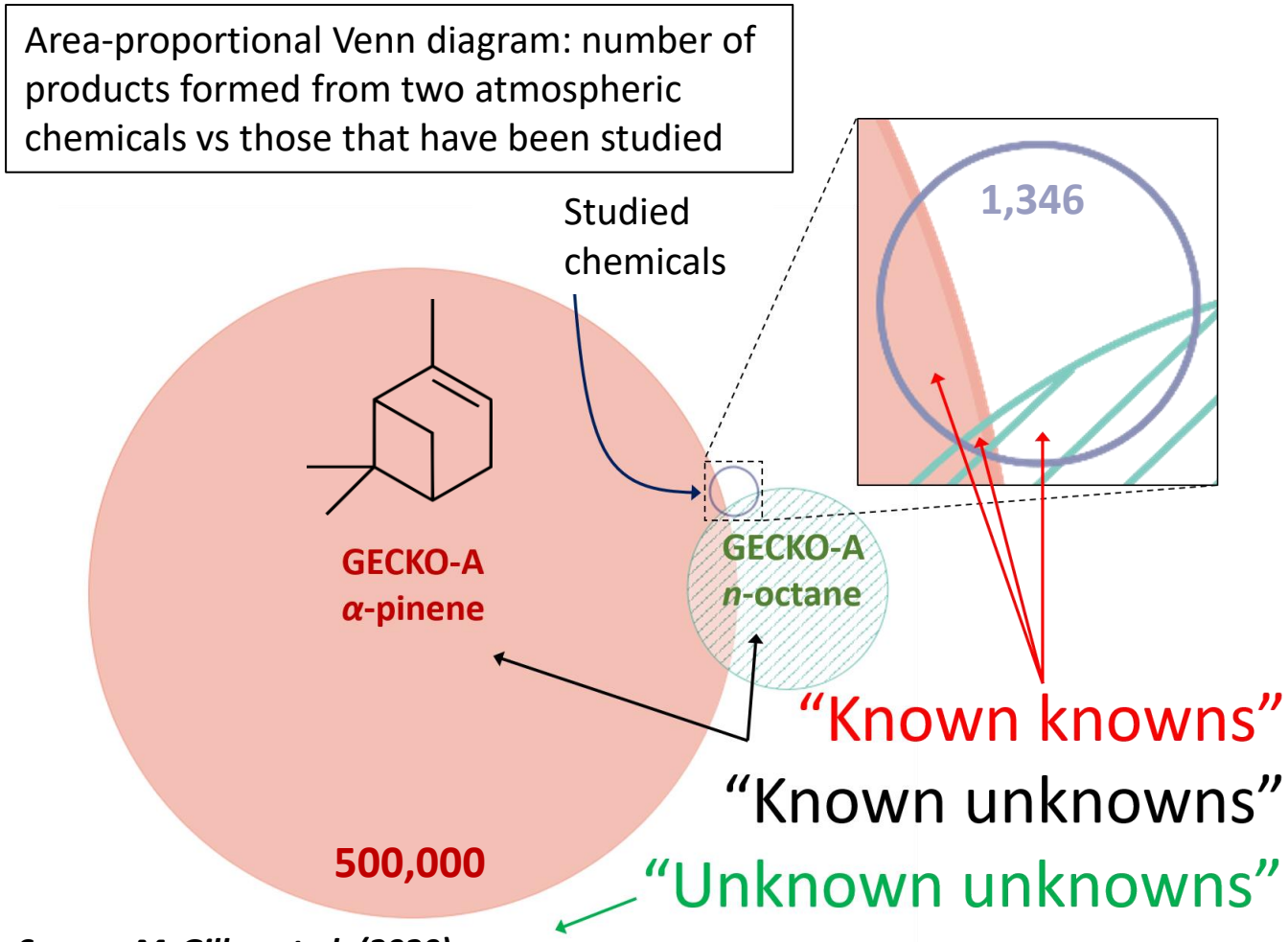
Pressure dependence in ozonolysis



- 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)



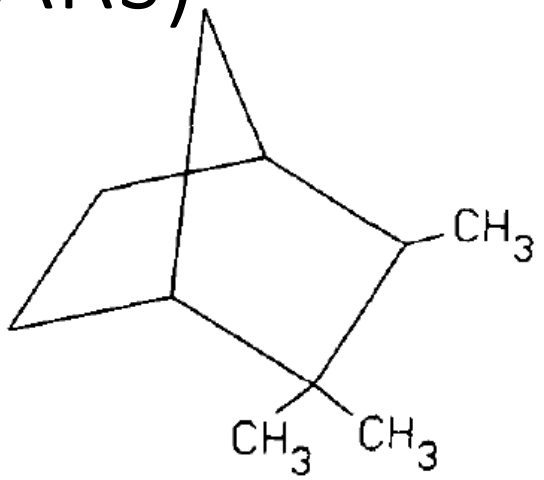
Source: McGillen et al. (2020)

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



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

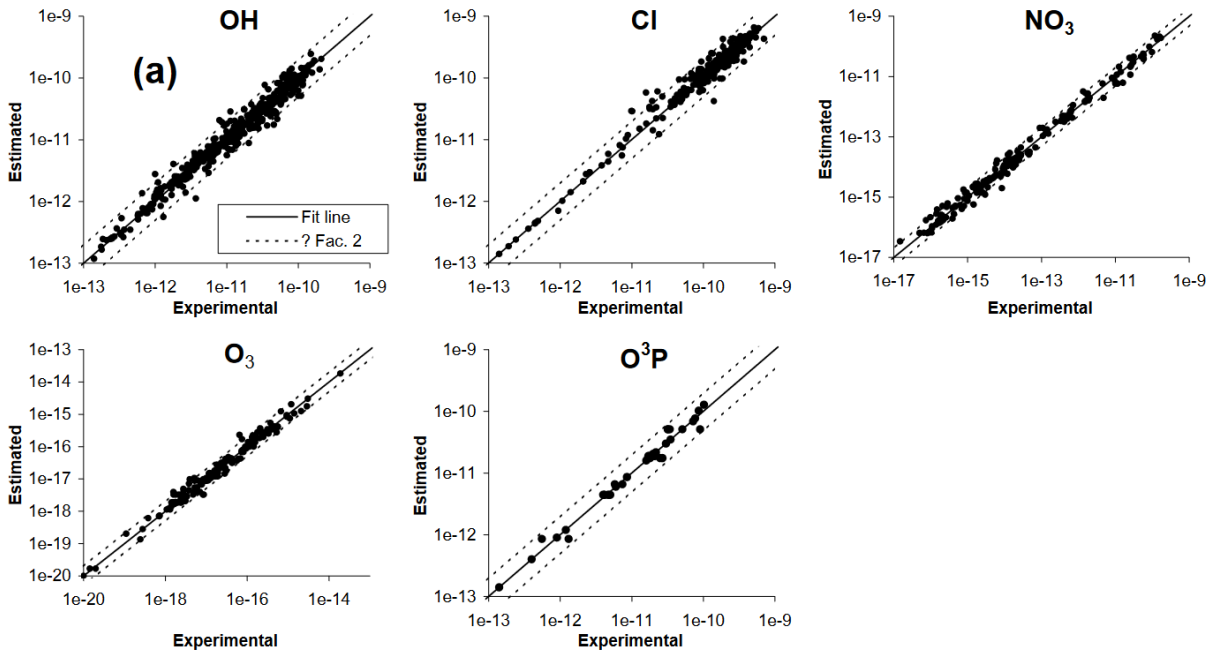
Example calculation from: Kwok and Atkinson (1995)

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: $RH + OH \rightarrow H_2O + R$, a description of the strength of the R–H bond may be best
- On the other hand, for OH addition reactions: $R_1(R_2)C{=}C(R_3)R_4 + OH \rightarrow R_1(R_2)(OH)C{=}C(R_3)R_4$, 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 ~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/

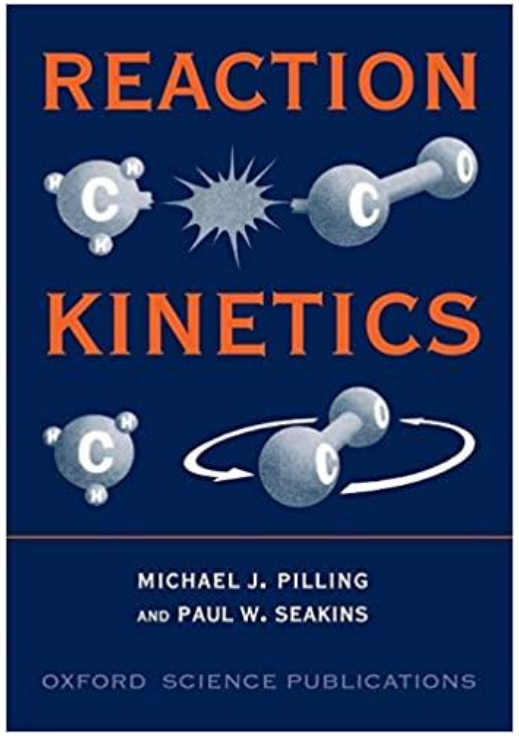
IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation:
https://iupac-aeris.ipsl.fr/

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