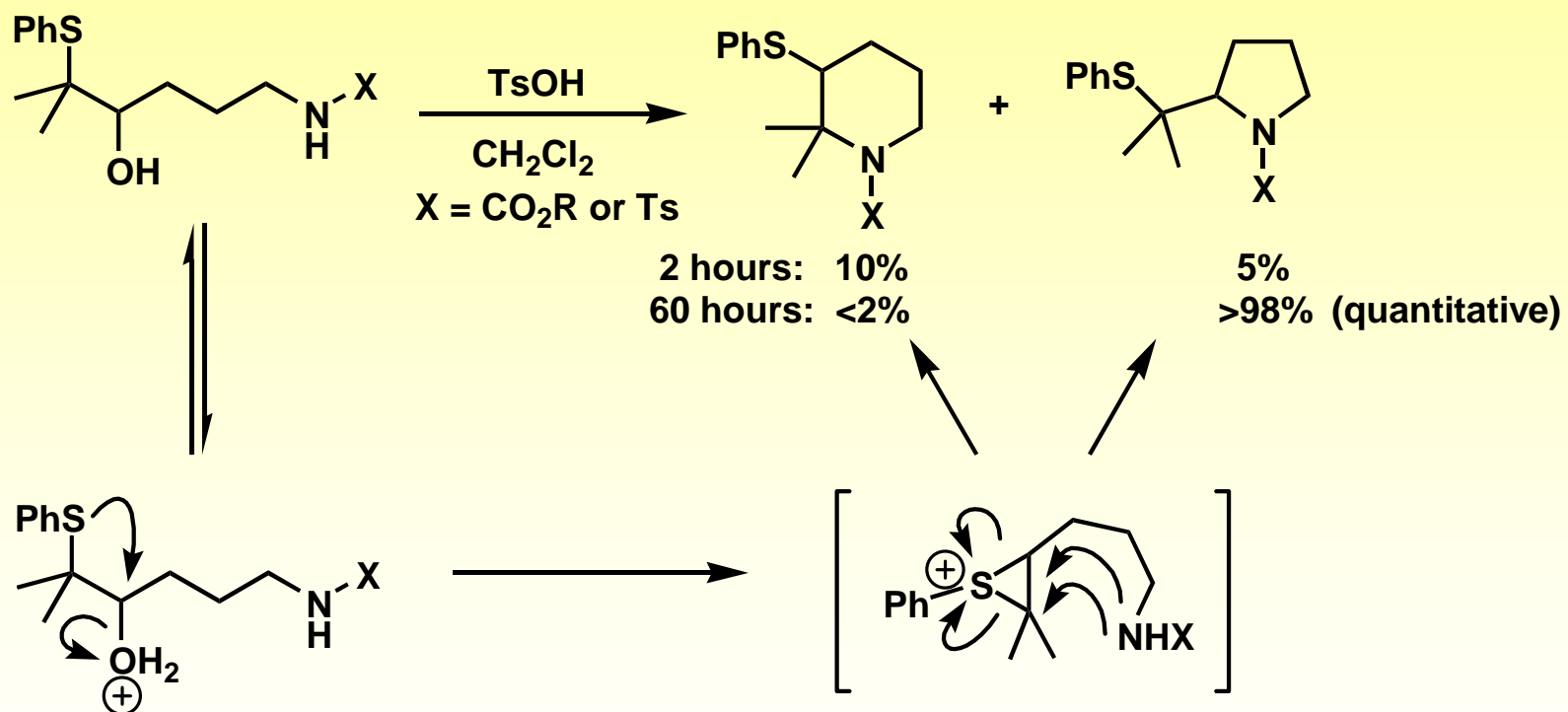


Taking POC for SOC further

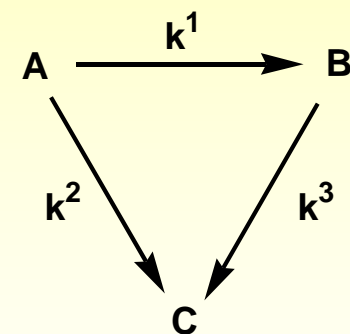
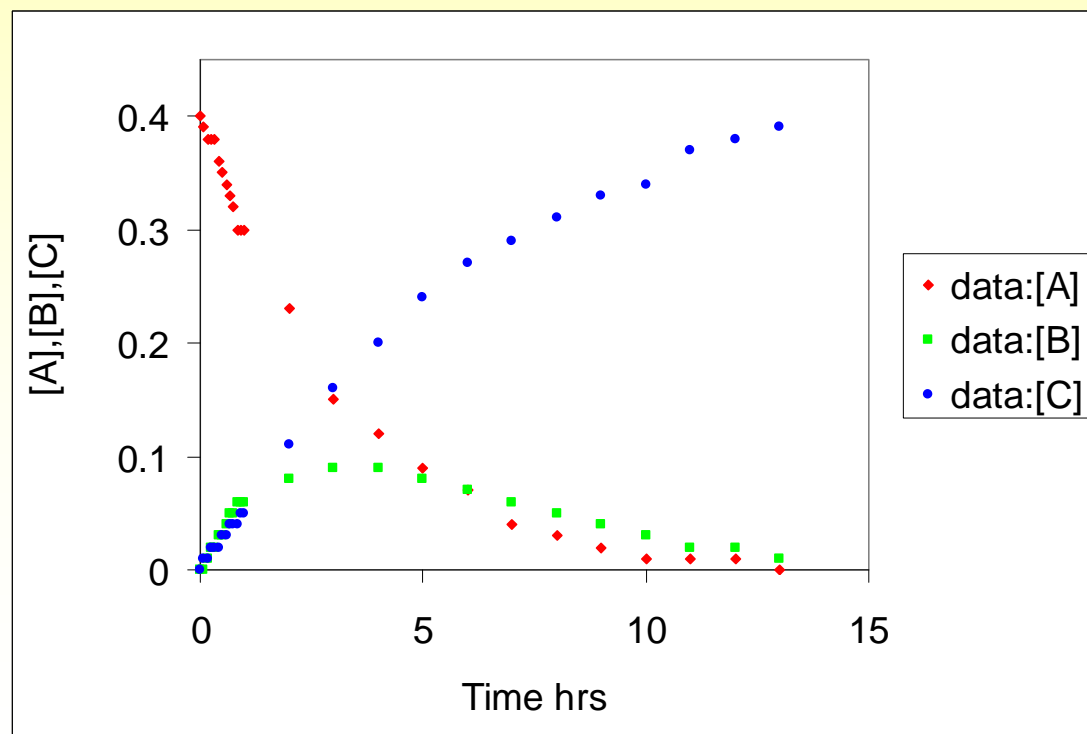
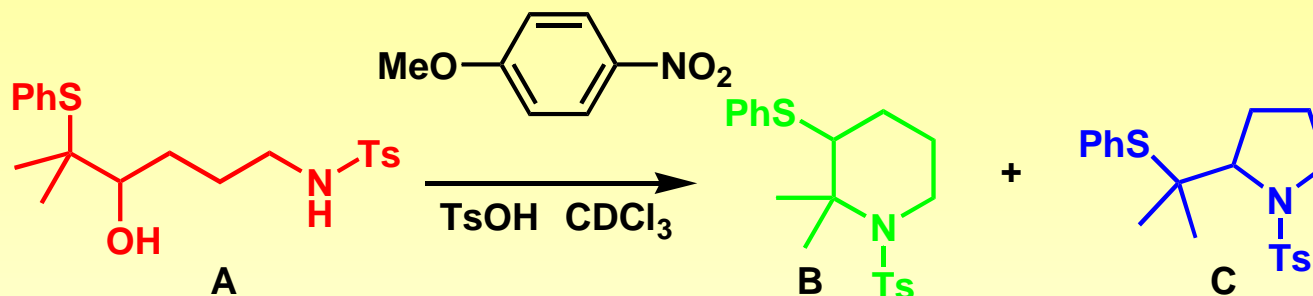
Contents

- Complex systems
- Solving analytically
- Solving numerically
- Catalytic cycles
- Rate-determining steps
- Changes in R.D.S.
- D.F.T. is support of mechanisms
- Correlation with kinetic data

Episulfonium-ion mediated ring closure



Episulfonium-ion mediated ring closure

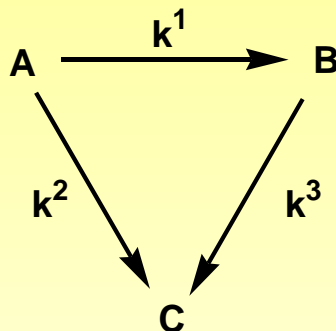


$$\frac{d[A]}{dt} = -k^1 [A] - k^2 [A]$$

$$\frac{d[B]}{dt} = k^1 [A] - k^3 [B]$$

$$\frac{d[C]}{dt} = k^2 [A] + k^3 [B]$$

Integrated rate expressions



$$\frac{d[A]}{dt} = -k^1 [A] - k^2 [A]$$

$$[A] = [A]_0 e^{-(k^1+k^2)t}$$

$$\frac{d[B]}{dt} = k^1 [A] - k^3 [B]$$

$$[B] = \frac{k_1 [A]_0}{k_3 - k_1 - k_2} \left(e^{-(k^1+k^2)t} - e^{-k^3 t} \right)$$

$$\frac{d[C]}{dt} = k^2 [A] + k^3 [B]$$

$$[C] = [A]_0 \left(1 - e^{-(k^1+k^2)t} - \frac{k_1}{k_3 - k_1 - k_2} \left(e^{-(k^1+k^2)t} - e^{-k^3 t} \right) \right)$$

Is it possible to do this without the integration?

YES! Euler's method for solving differential equations numerically.

1) We know the simple rate expressions.

2) Take a guess at the rate constant k

3) We know $[A]$ and we know $\frac{d[A]}{dt}$

4) Start at " t^1, A^1 " and move a small time step δt in direction of gradient

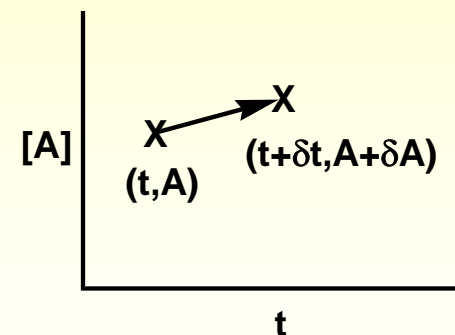
5)
$$\delta A = \frac{d[A]}{dt} \delta t$$

6) Calculate $t^1 + \delta t = t^2$ and calculate $A^1 + \delta A = A^2$.

7) Repeat again and again until $t = \text{end of reaction}$

8) Compare the calculated values of A with the experimental values of A . Calculate RMS error.

9) Repeat with a new values of rate constant k until error is minimised.



Is it possible to do this without the integration?

Actually the 4th Order Runge Kutta method is better. And there is plug-in for Excel:

http://www.chem.mtu.edu/~tbco/cm416/RK4_v3_0.html or Google "excel rk4 plug in"

1) Download and install plug-in

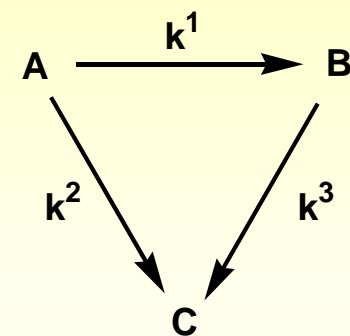
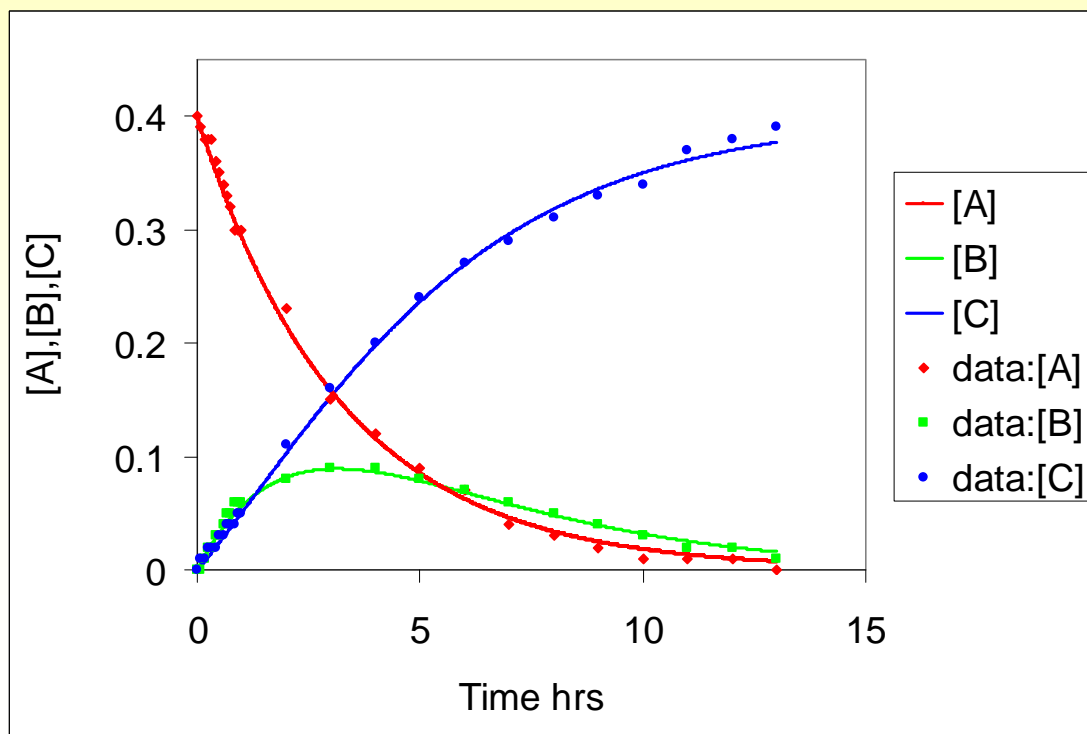
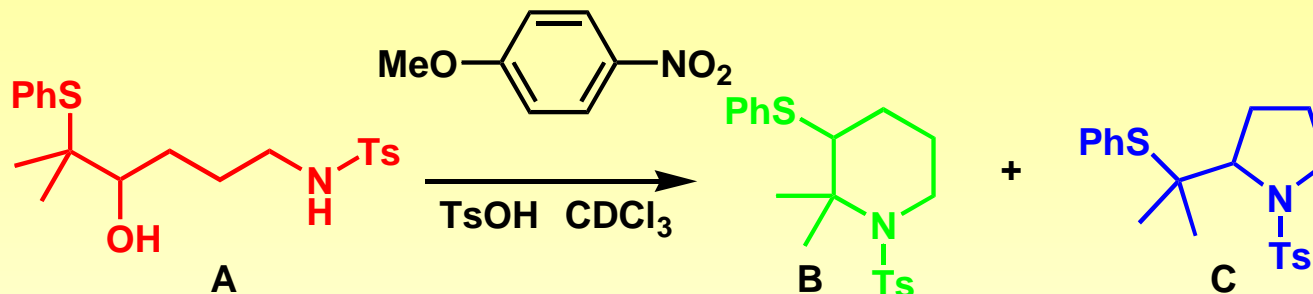
2) Get your rate constants and starting concentrations into a .rk4 file (see guide): [Sarah.rk4](#)

3) Get your data into .dat file: [Sarah8.dat](#)

4) Open Excel and press the RK4 button. [Blank.xls](#)

[XLfile2](#)

Using RK4 numerical method



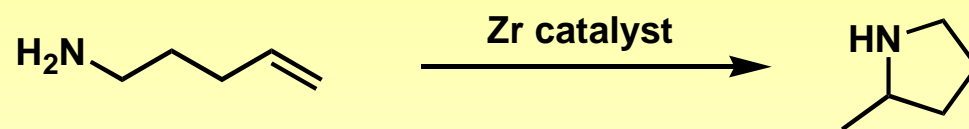
$$k^1 = 0.193$$

$$k^2 = 0.116$$

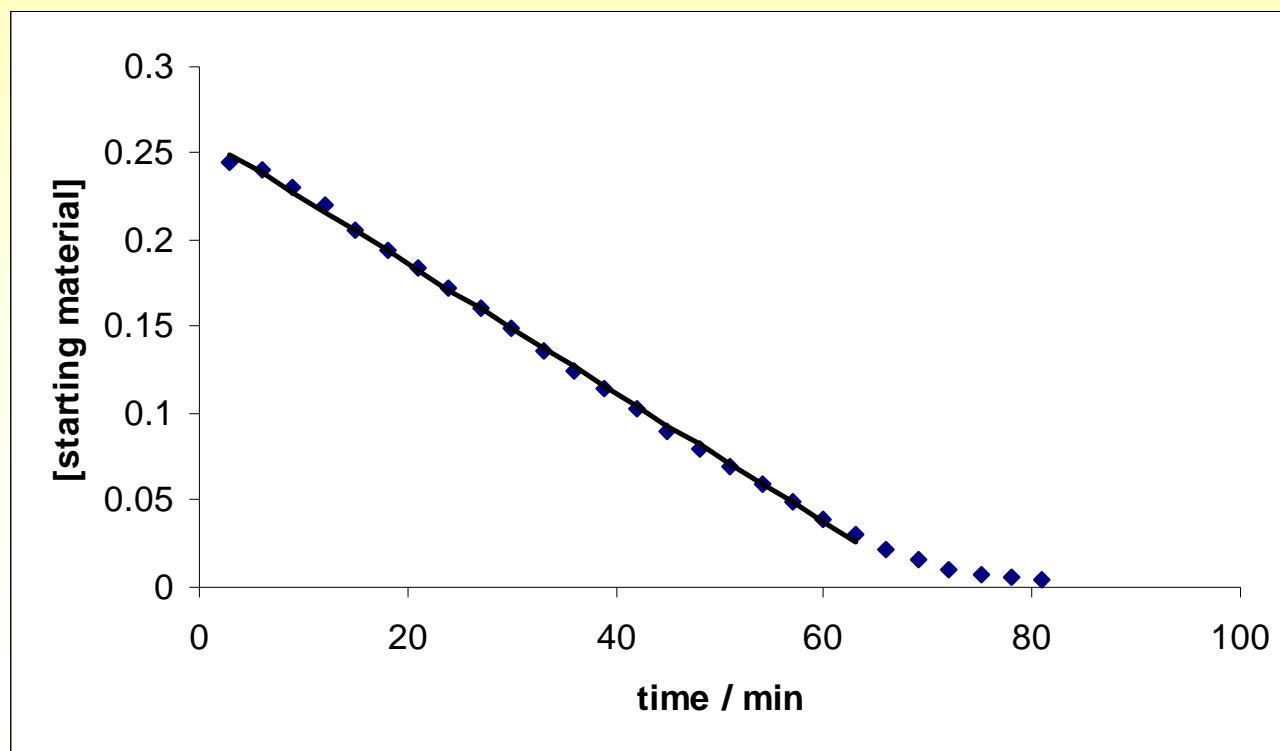
$$k^3 = 0.329$$

$$\text{RMS error} = 0.006035$$

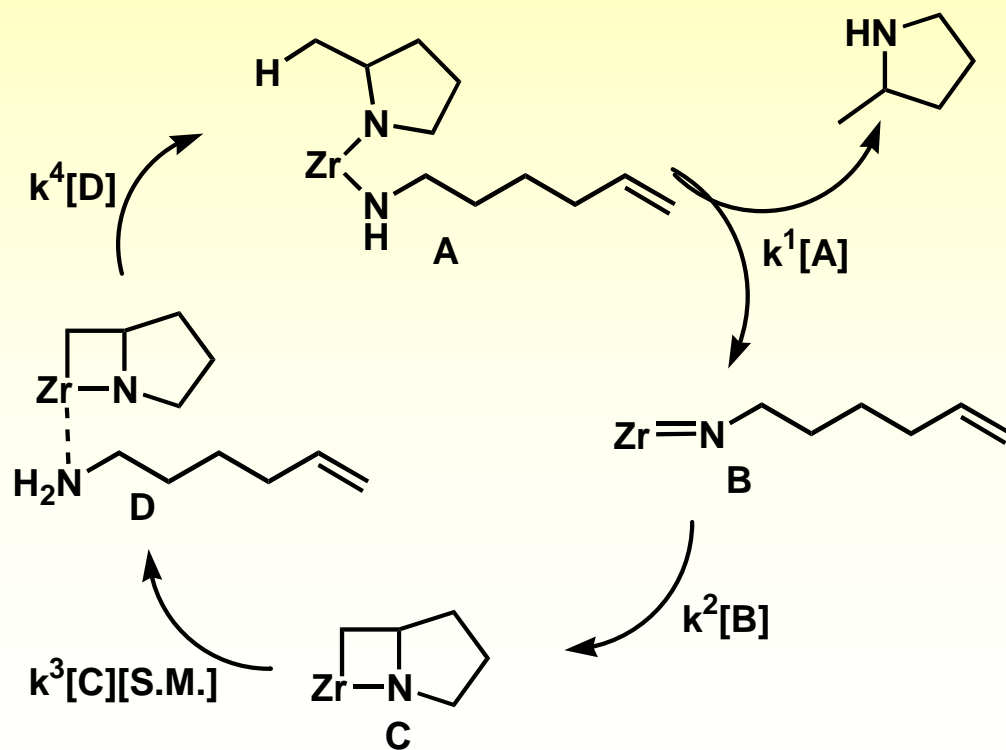
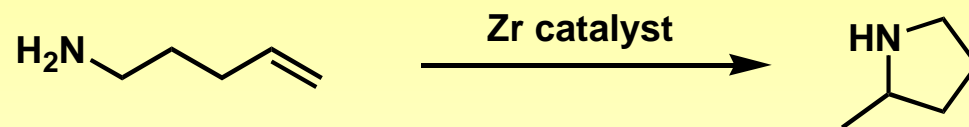
Catalysis kinetics



Scott group
@ Warwick

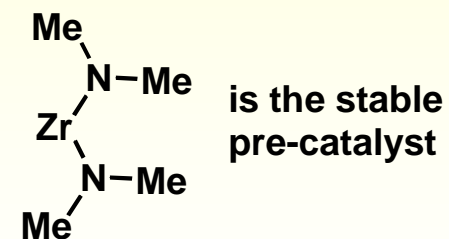


Catalytic cycles



$$\frac{d[\text{prod}]}{dt} = \text{constant}$$

rate determining step
must not include free
amine starting material



so A is resting state and

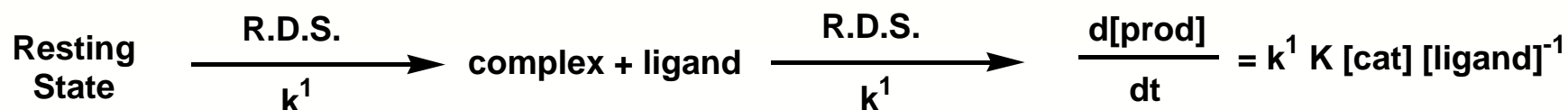
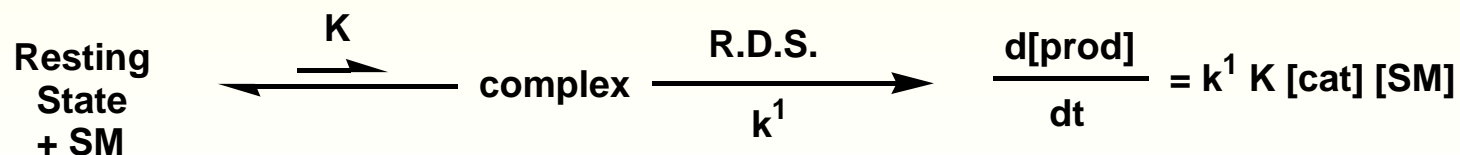
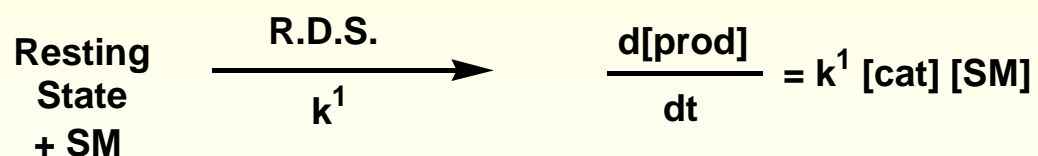
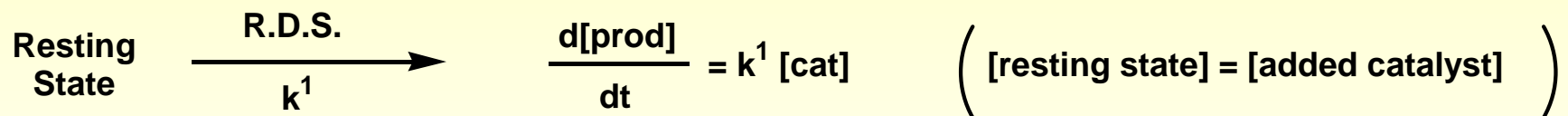
$$\frac{d[\text{prod}]}{dt} = k^1 [\text{Zr}]$$

Zero order in SM

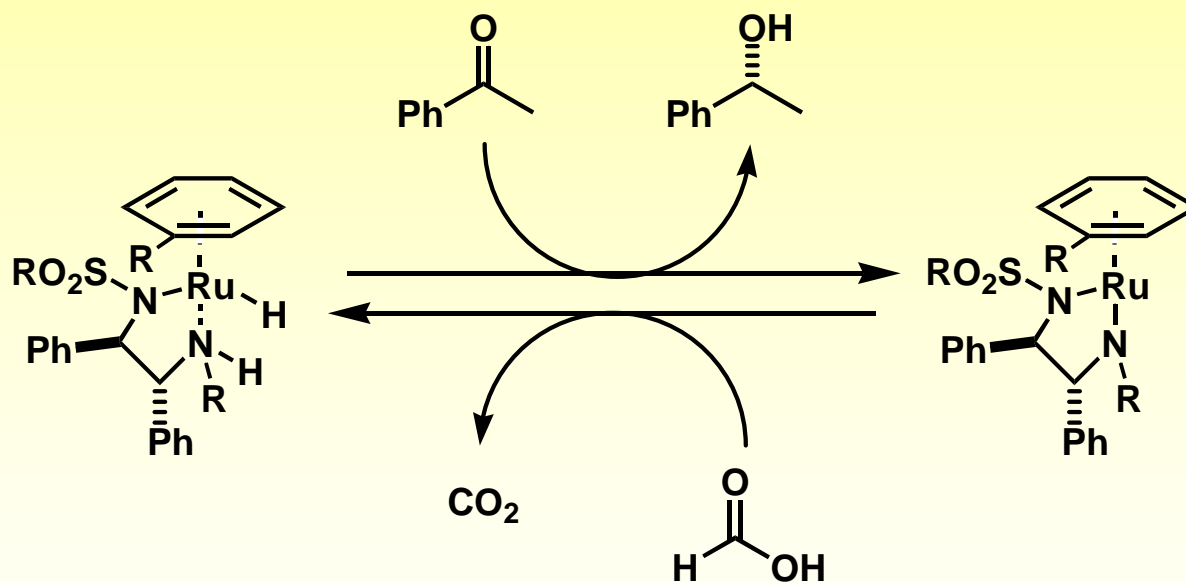
Catalysis kinetics

For a non-catalytic reaction: the reaction rate expression describes the difference in atomic make up between the starting materials and rate determining step

For a catalytic reaction: the reaction rate expression describes the difference in atomic make up between the catalyst resting state and rate determining step

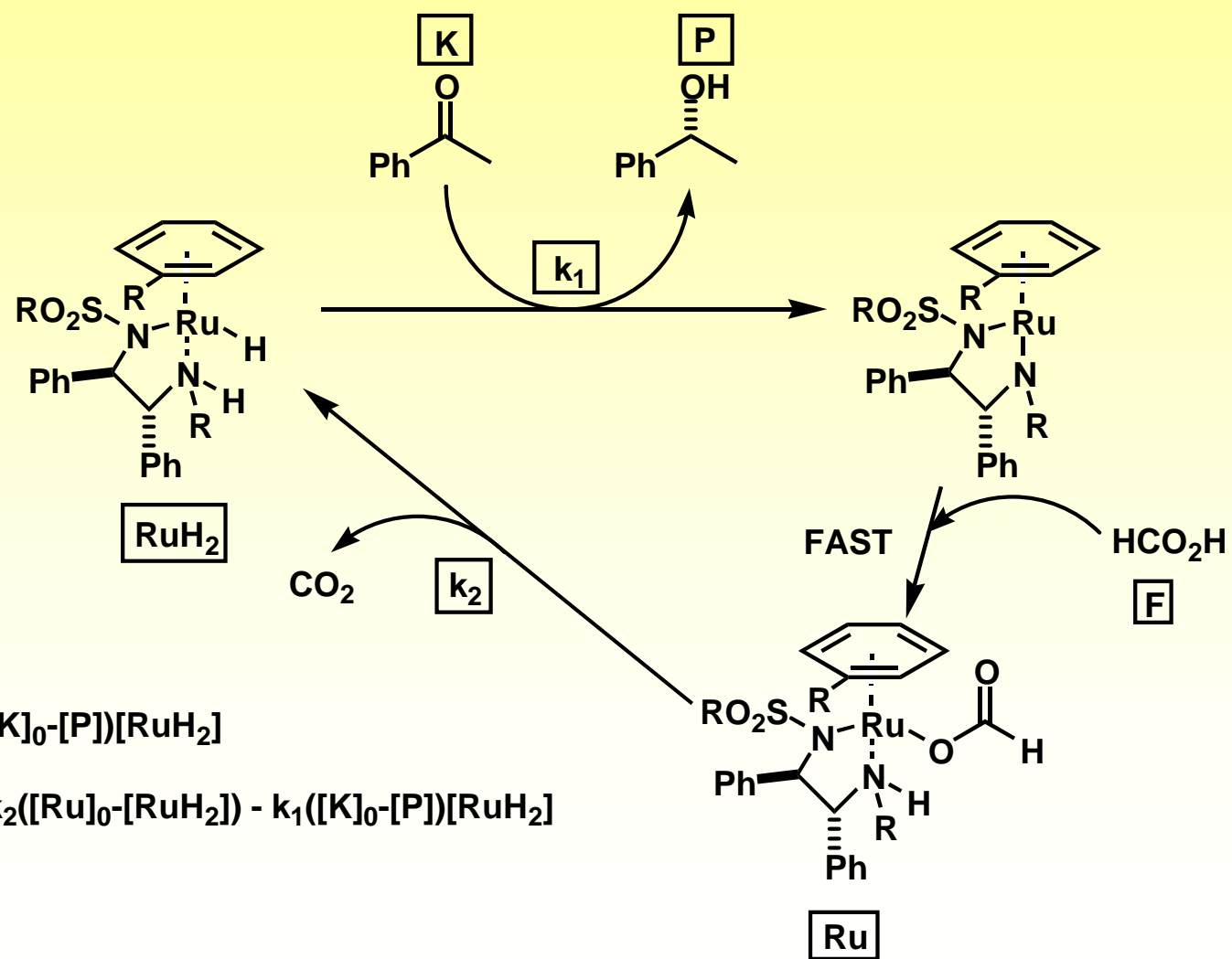


Changes in Rate-determining step

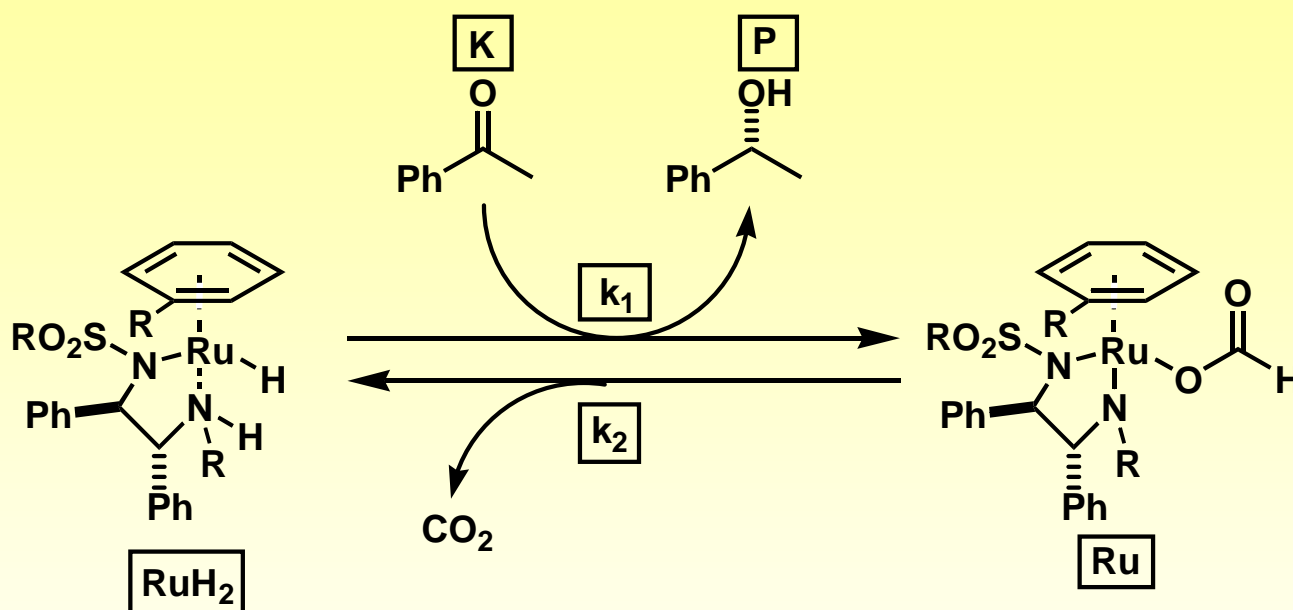


Noyori, Wills and others

Reaction mechanism and kinetics



Reaction mechanism and kinetics

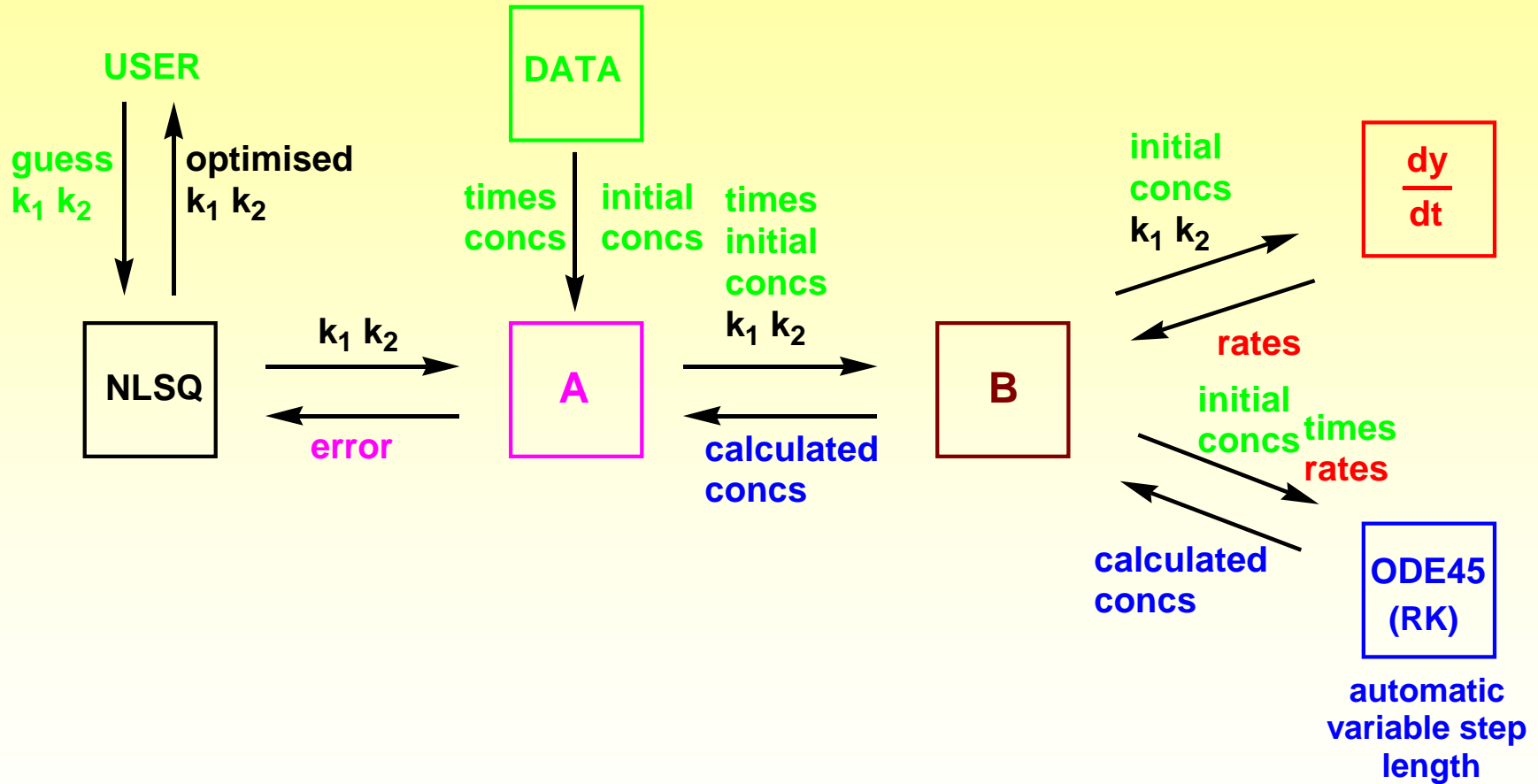


$$\frac{d[\text{P}]}{dt} = k_1([\text{K}]_0 - [\text{P}])[\text{RuH}_2]$$

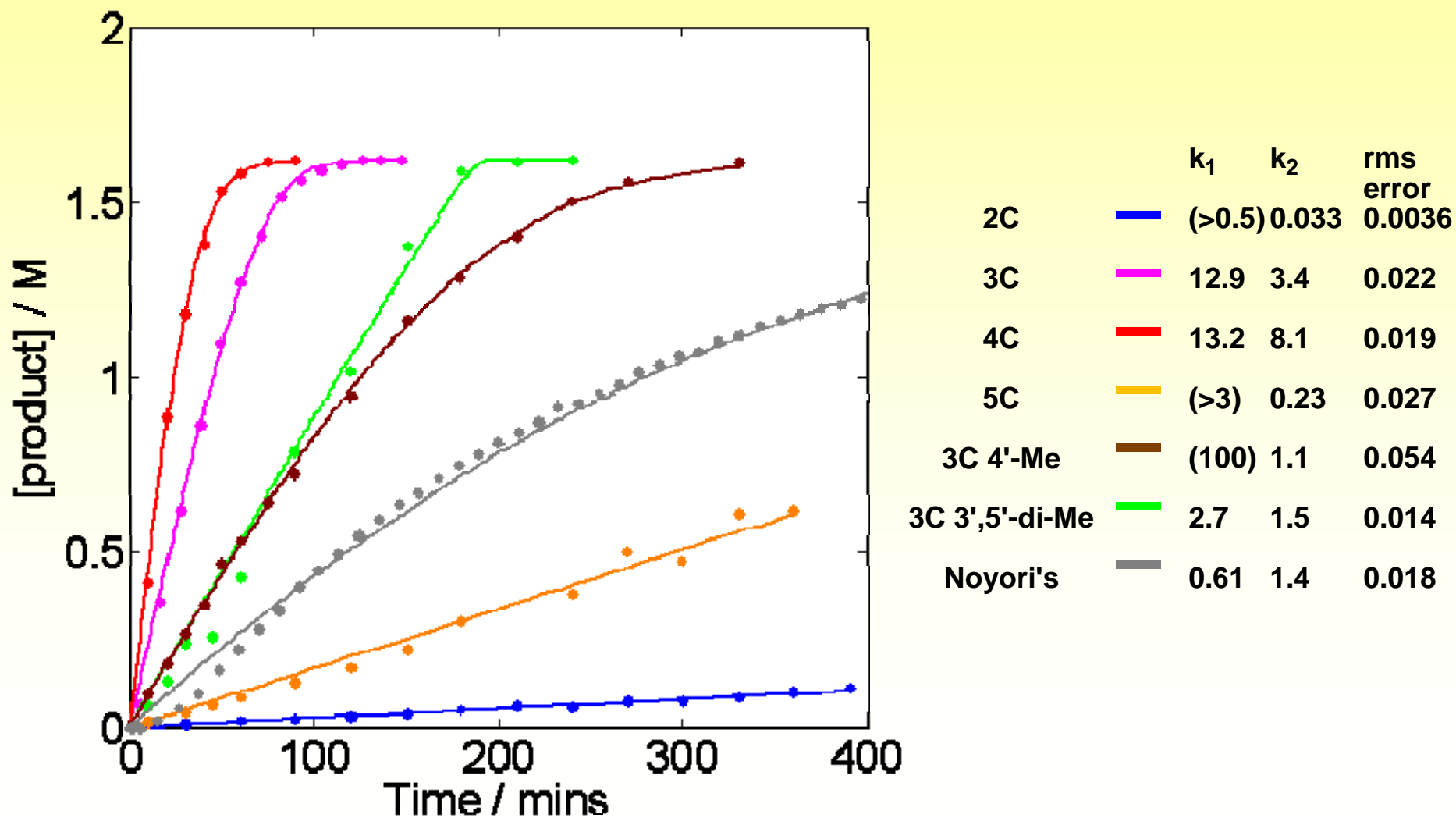
$$\frac{d[\text{RuH}_2]}{dt} = k_2([\text{Ru}]_0 - [\text{RuH}_2]) - k_1([\text{K}]_0 - [\text{P}])[\text{RuH}_2]$$

Coupled differential equations: $d[\text{P}]/dt$ and $d[\text{RuH}_2]/dt$ as functions of $[\text{P}]$, $[\text{RuH}_2]$ and constants.

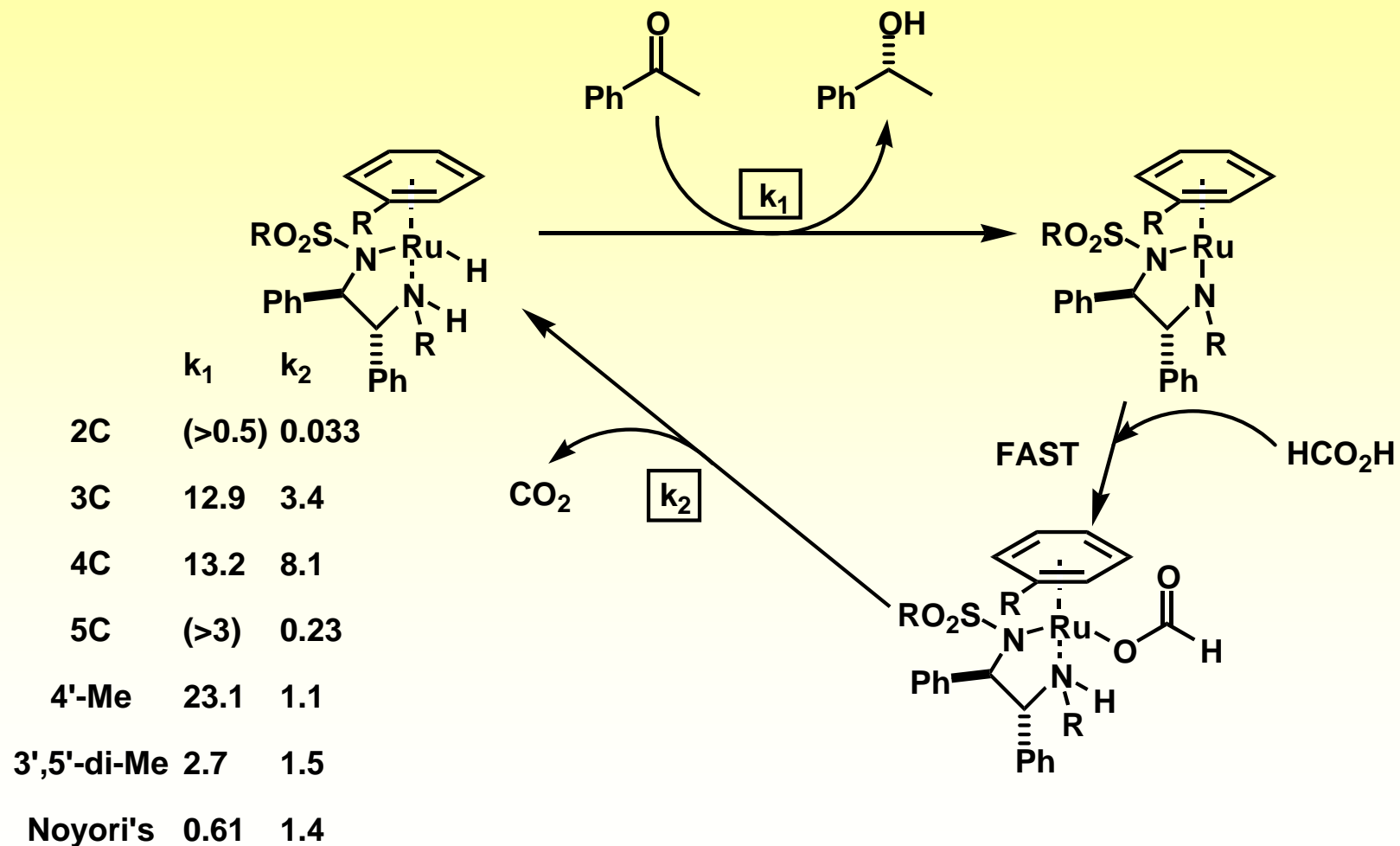
Solving coupled differential equations using MATLAB



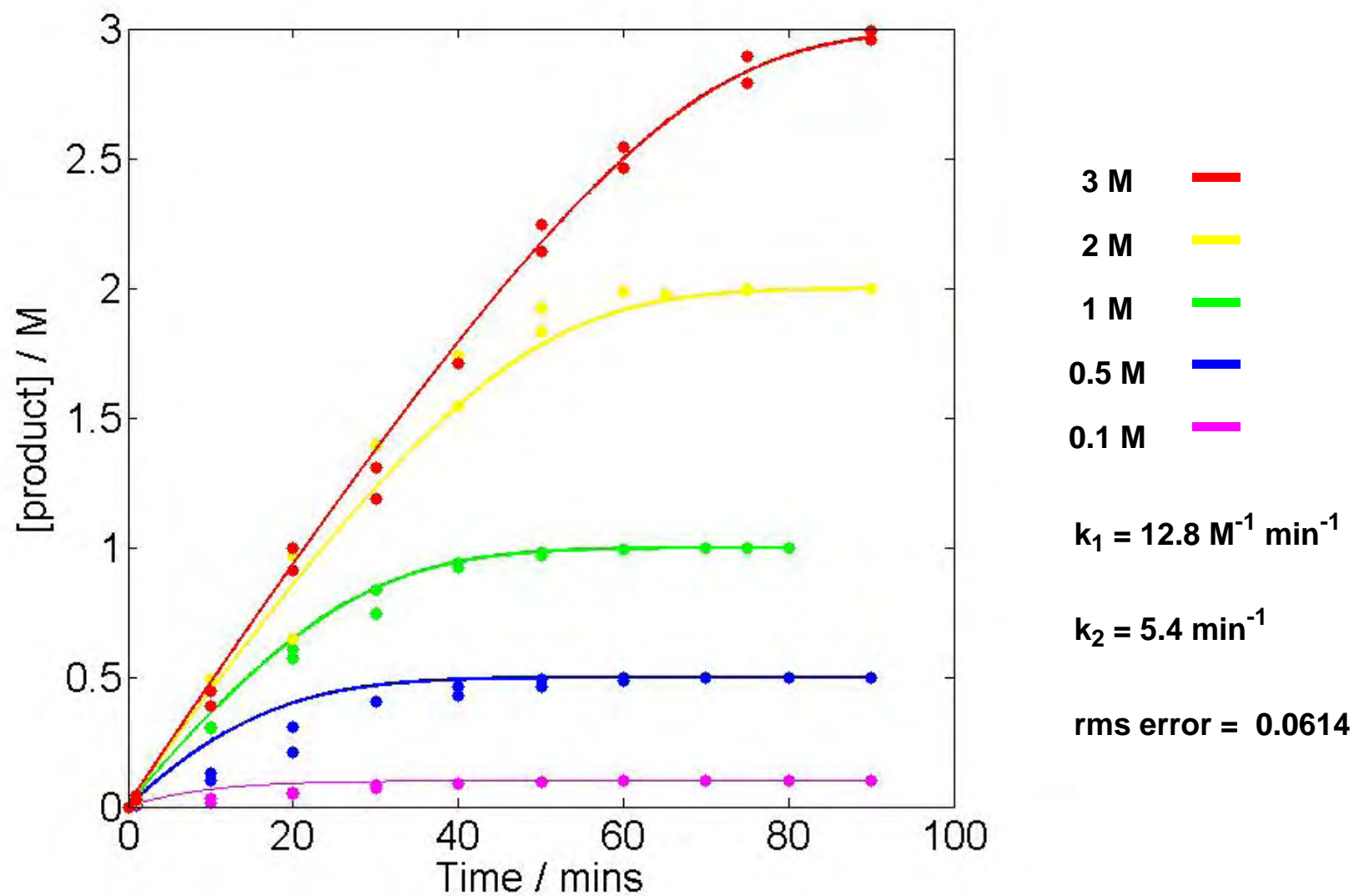
Data from GC and NMR for various catalysts



Data from GC and NMR for various catalysts



Changes in RDS due to starting concentrations

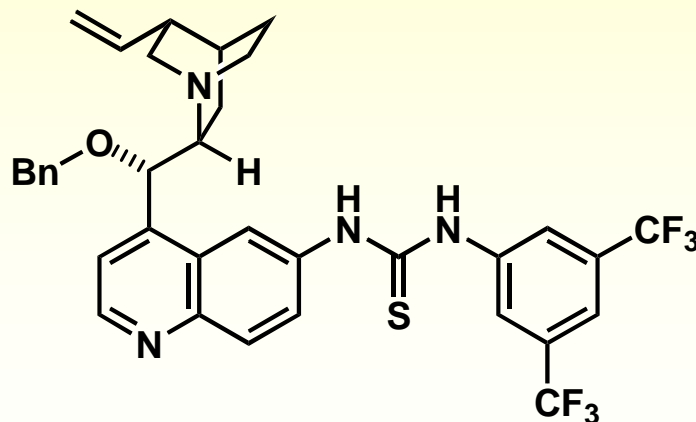
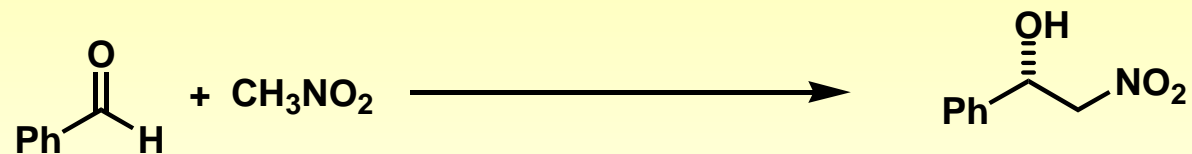


Using modelling to help with TS structure

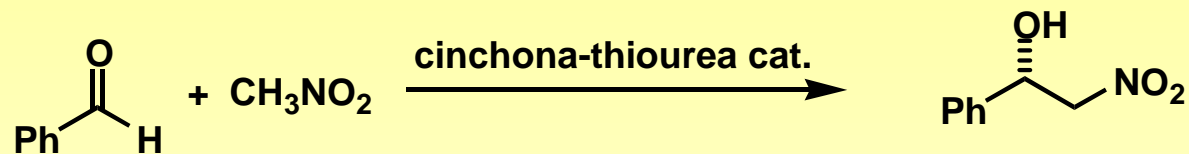
Kinetics can tell you the atoms in the transition state of the RDS. What about the structure?

Quantum chemical calculations can really help in modelling the structure of the transition state.

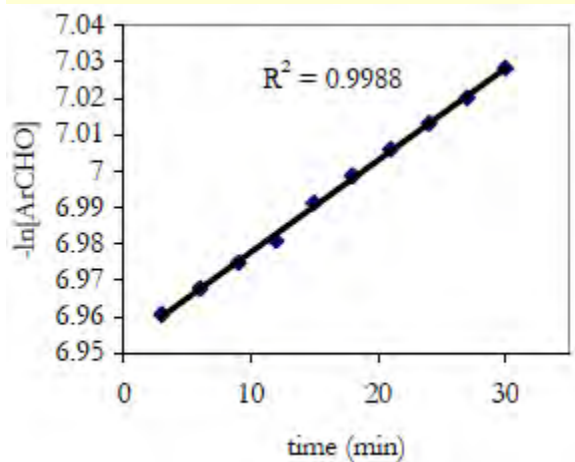
e.g.



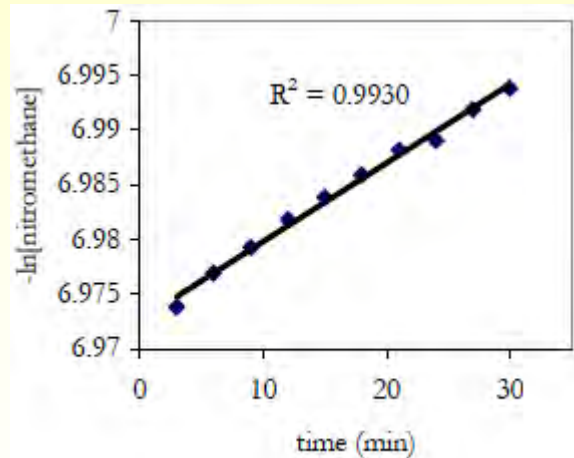
What is in the T.S.?



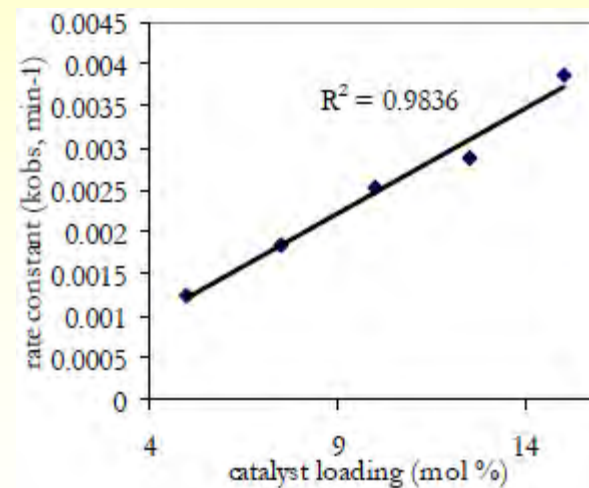
1st order in
aldehyde



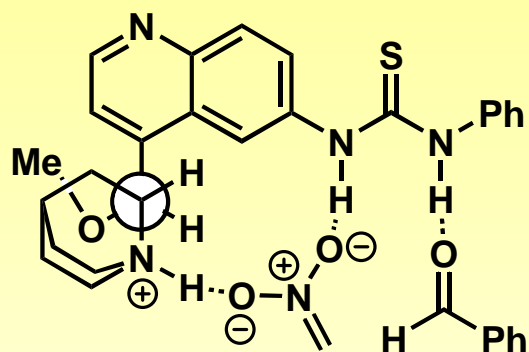
1st order in
nitromethane



1st order in
catalyst

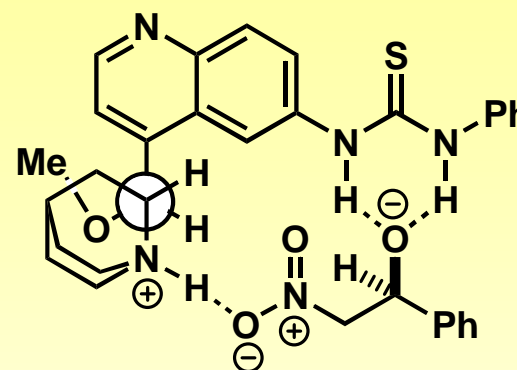


Competing pathways

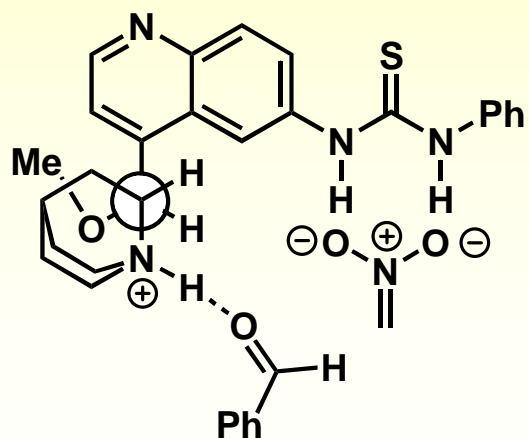


Starting material complex

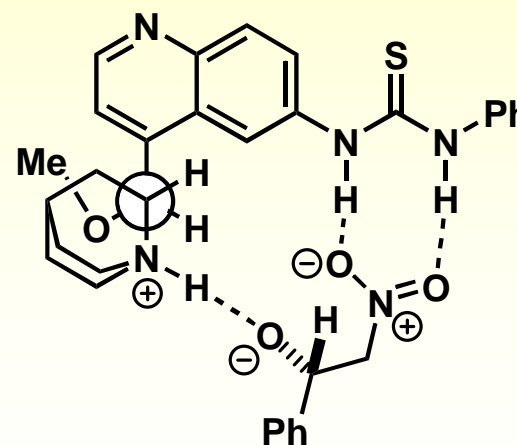
Lower energy pathway



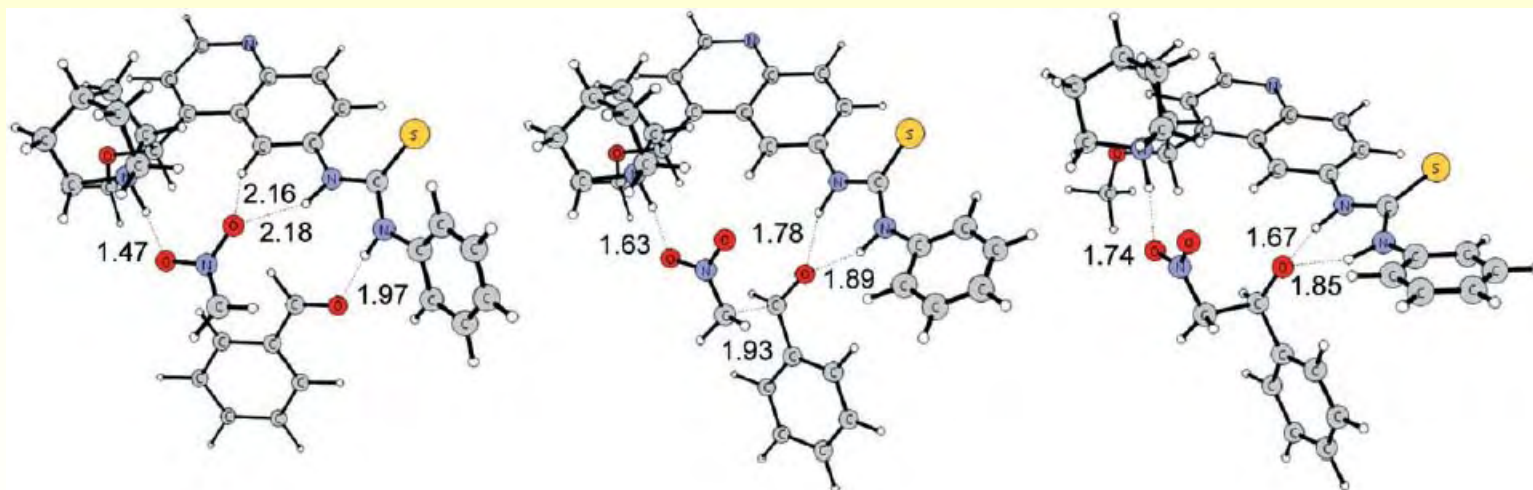
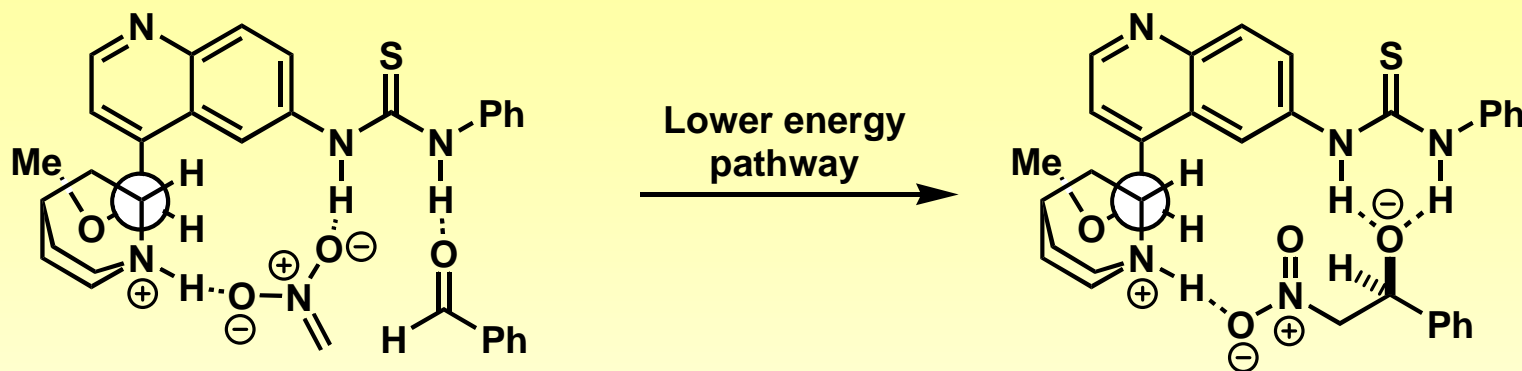
Product complex



Higher energy pathway



Modelling the reaction path

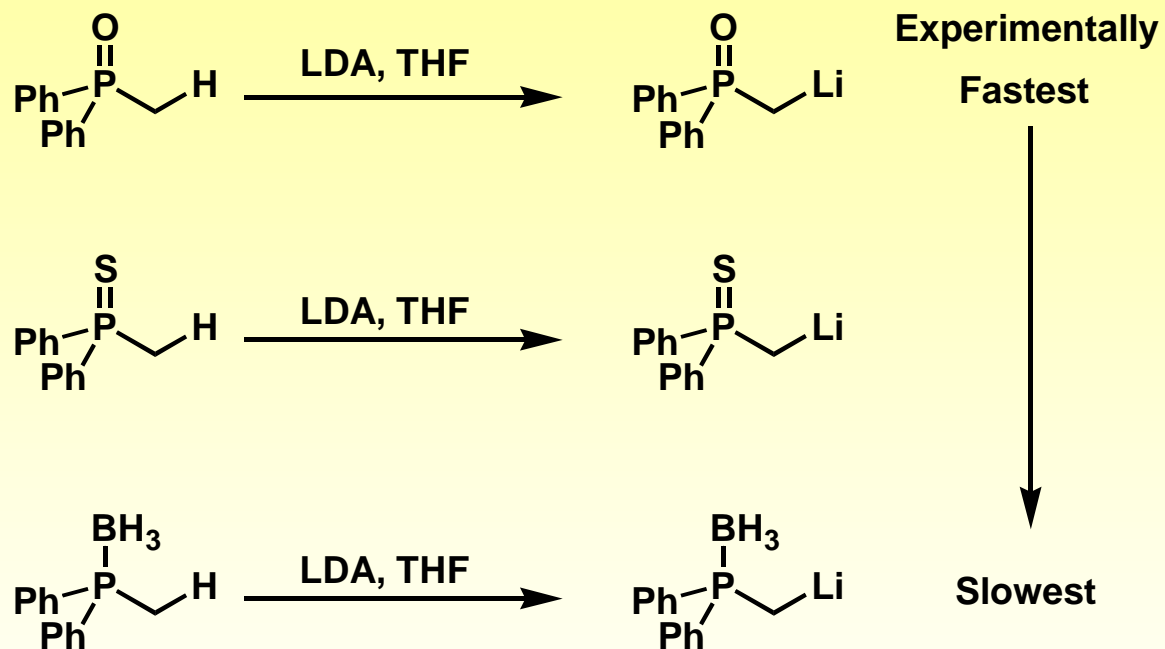


Starting complex
G.S.

Reaction
T.S.

Product complex
G.S.

Modelling relative rates



Can we use modelling (DFT) to help understand why?

Getting started in DFT

Commerical software such as Gaussian and Jaguar are widely used (but expensive).

GAMESS and **PCGAMESS** / Firefly are free!

PCGAMESS is available for windows, mac and linux, and it fast.

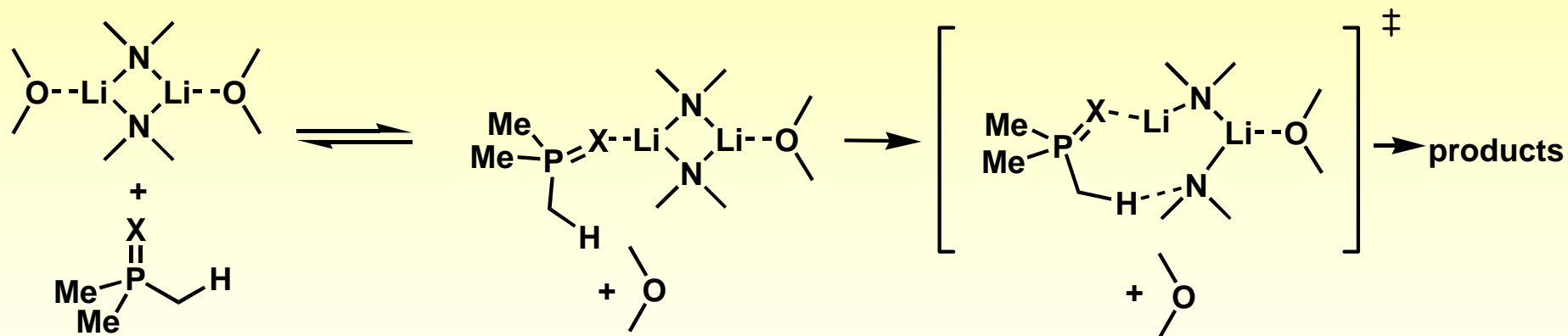
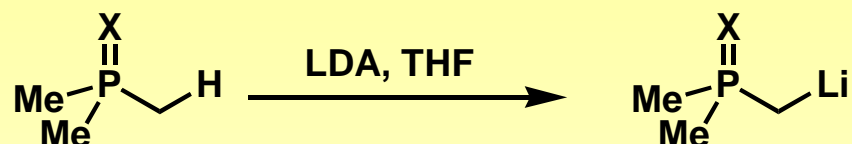
Instructions are included and it is simple to set up and use.

Helpful points:

Start on simple systems.

Build up complex systems from the reaction site outwards (particularly for T.S. calcs).

Modelling relative rates

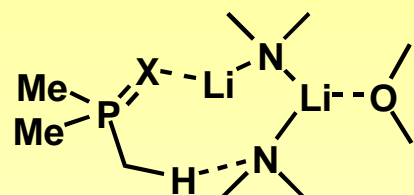


O	0 kJ / mol	→	O	- 24.7 kJ / mol	$\xrightarrow{+60.5}$	O	+35.8 kJ / mol
S	0 kJ / mol	→	S	+16.7 kJ / mol	$\xrightarrow{+57.7}$	S	+74.4 kJ / mol
BH ₃	0 kJ / mol	→	BH ₃	+22.2 kJ / mol	$\xrightarrow{+66.4}$	BH ₃	+88.6 kJ / mol

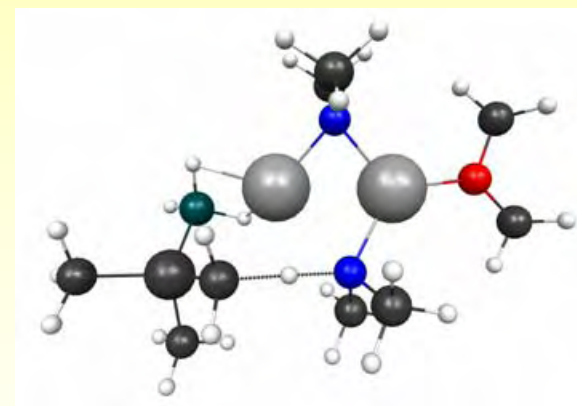
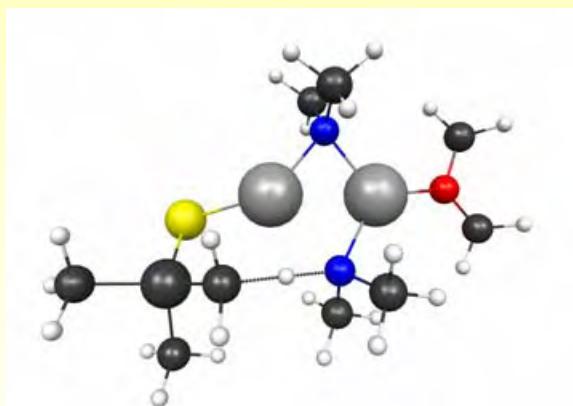
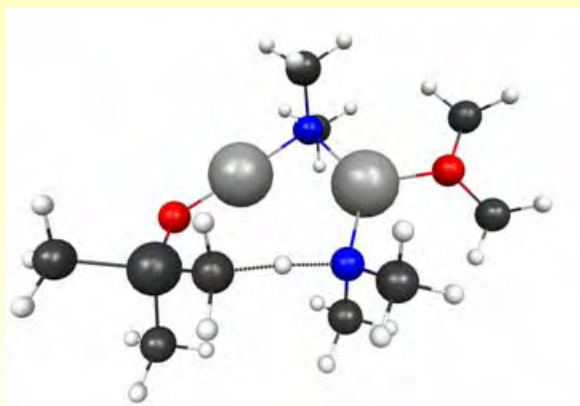
For each X (O, S, BH₃)
set combined SM
energy to zero

Conclusion: binding to Li dominates

Modelling relative rates

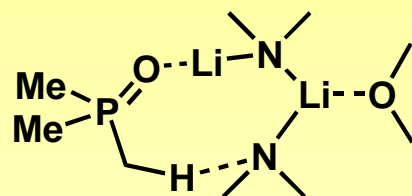


O	+35.8 kJ / mol	} relative to their own respective uncomplexed starting material
S	+74.4 kJ / mol	
BH ₃	+88.6 kJ / mol	

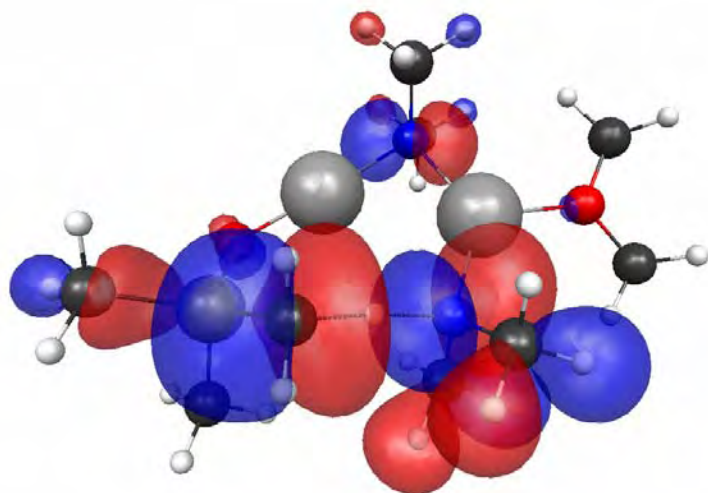


Pictures from MacMolPlt (also free)

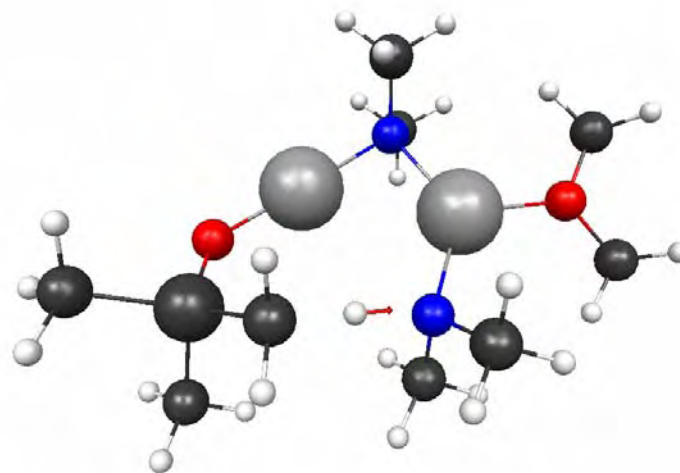
Modelling relative rates



HOMO of TS



Vector arrow of TS vibration



Pictures from MacMolPlt (also free)