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Mechanisms for the oxidation of aromatics: recent developments and remaining questions

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School of Chemistry

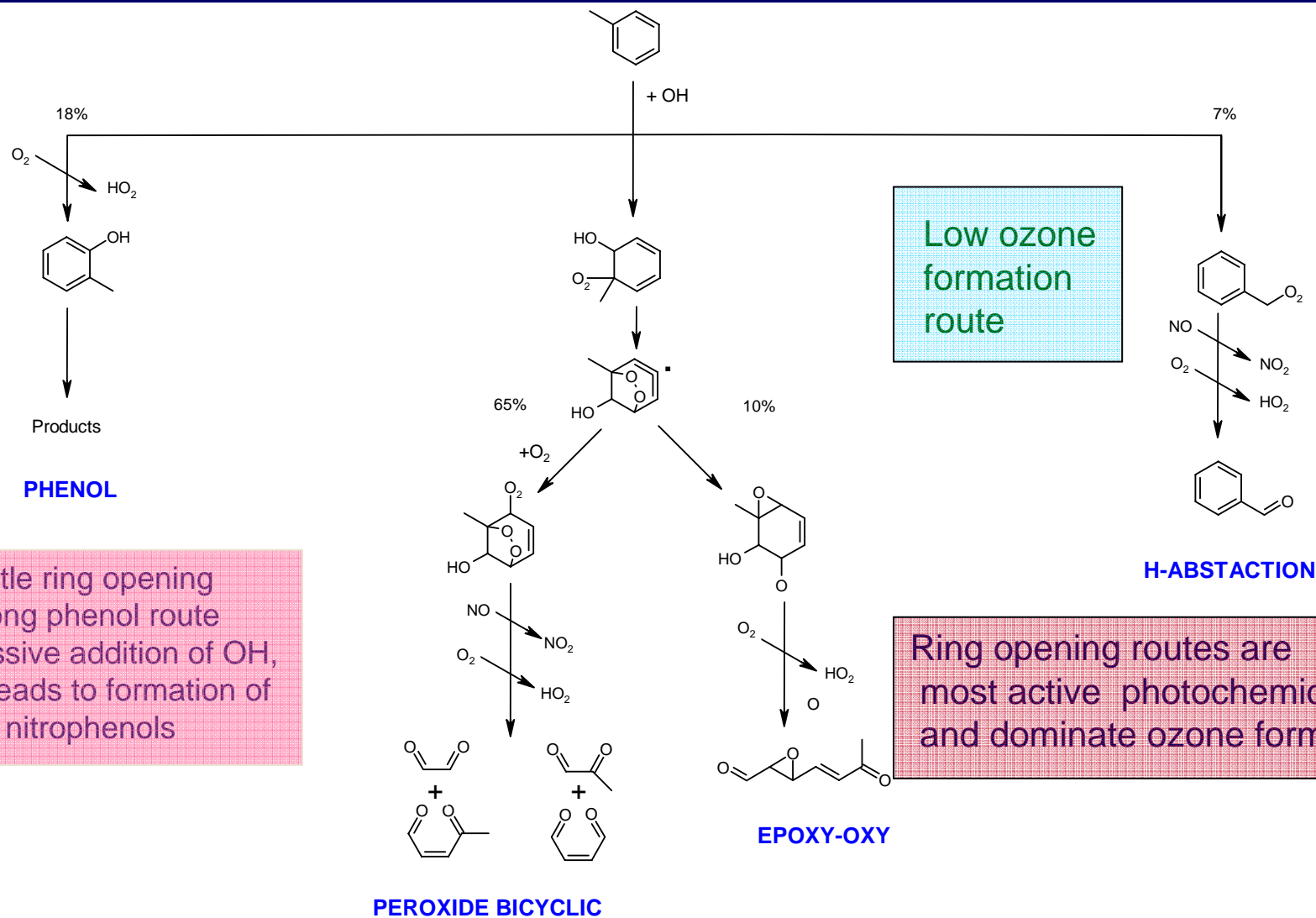
University of Leeds

Organics in the atmosphere, Vienna, October 7th 2008

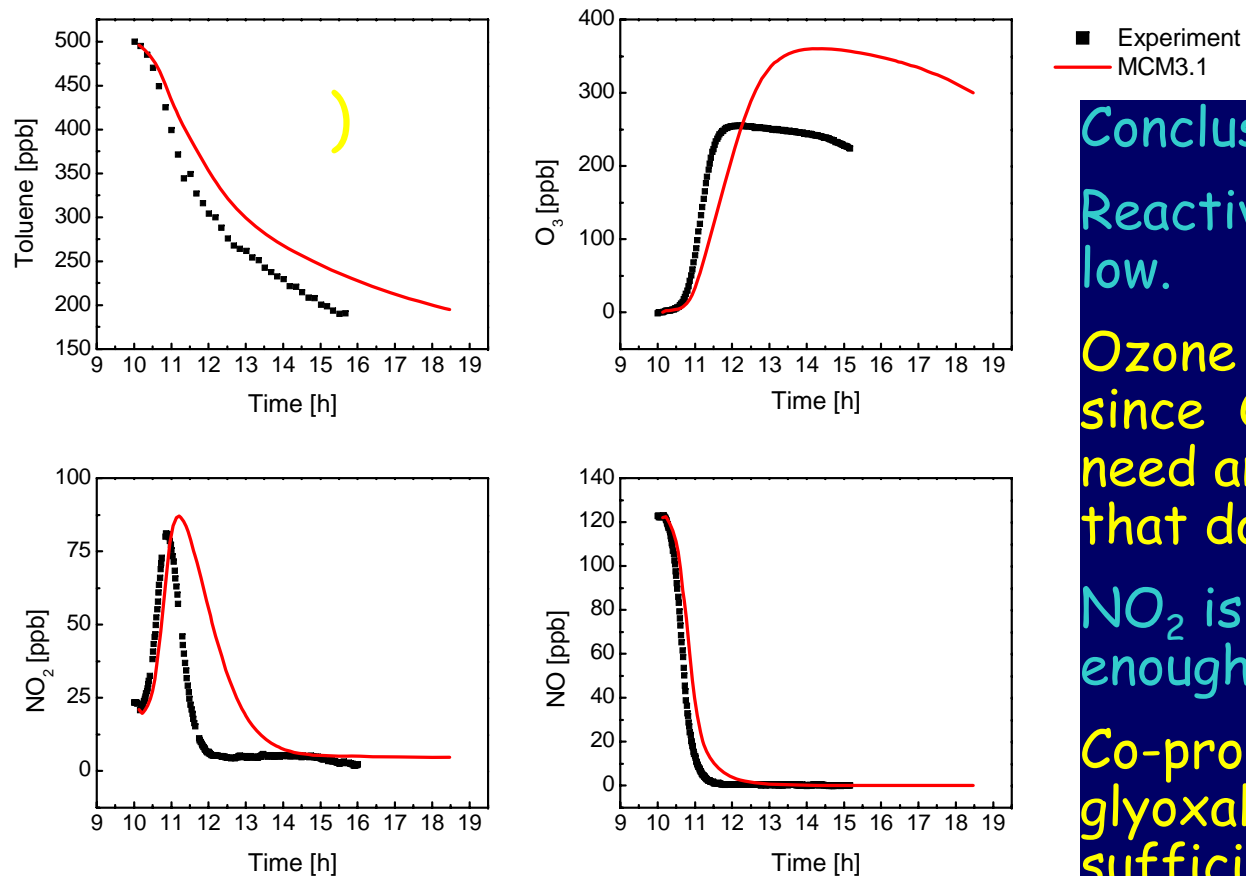
Synopsis

- Brief review of aromatic mechanisms
- Results on ring opening route from PSI, Leicester, CEAM.
- Electronic structure / master equation calculations from Leeds, designed to interpret and exploit experiments from Zetzsch and Lesclaux on very early stages of the process.
- Emphasis is placed on the links to a detailed, near-explicit mechanism, the master chemical mechanism, MCMv3.1

Toluene Oxidation Routes in MCMv3.1



EUPHORE: Comparison of MCM3.1 to Toluene Chamber Experiment (27/09/01)



Conclusions:

Reactivity (ie [OH]) is too low.

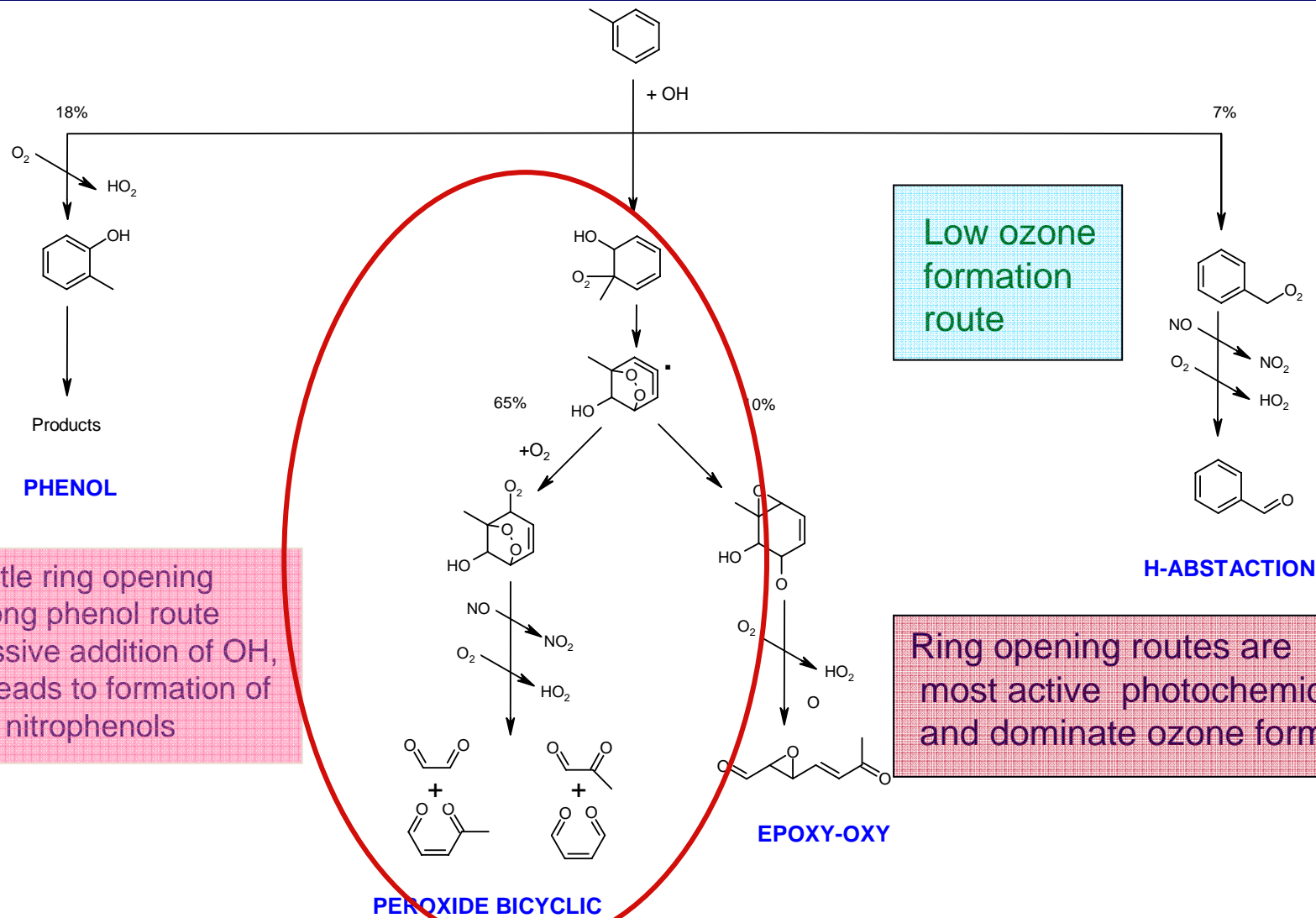
Ozone overpredicted, but since OH is too low, we need an early OH source that doesn't produce O₃

NO₂ is not removed rapidly enough

Co-products of glyoxal/Me glyoxal not detected in sufficient concn

Bloss et al, ACP 2005, 5, 623

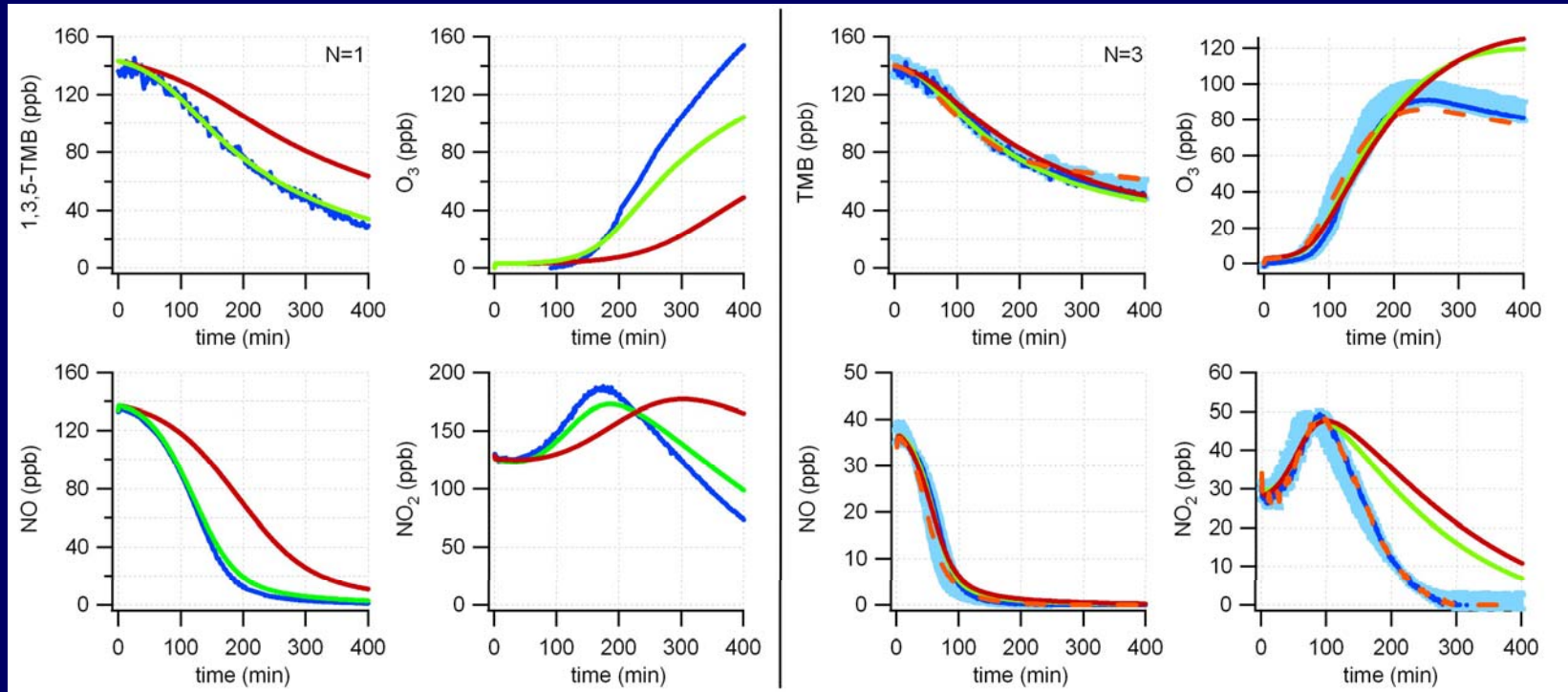
Toluene Oxidation Routes in MCMv3.1



Metzger et al, 1,3 5 trimethylbenzene: Evaluation of MCM
ACPD, 2008, 8, 11567 - 11607

- Chamber study at PSI- extensive analysis varying [TMB]/[NO_x] and [TMB].
- Comparison with MCM shows underestimation of TMB decay rate and hence of reactivity of system.
- [HONO] much higher than predicted. Attribute to
 $\text{NO}_2 + \text{light} \rightarrow \text{HONO}$ at chamber wall
- HONO photolysis then generates OH and increases reactivity

Metzger et al

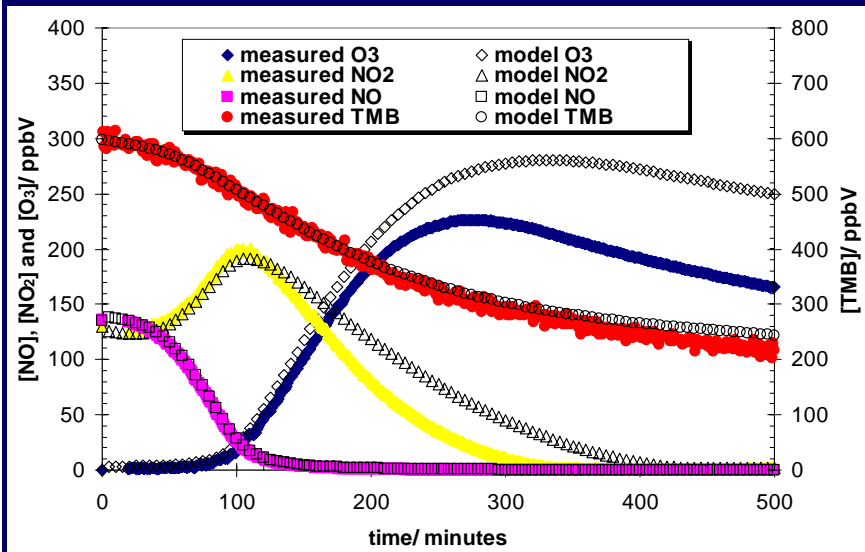


Model-measurement comparison for 1,3,5-trimethylbenzene, O₃, NO and NO₂ for low /medium concentration TMB experiments conducted at low (0.5, left) and medium (2, right) VOC/NO_x ratios.

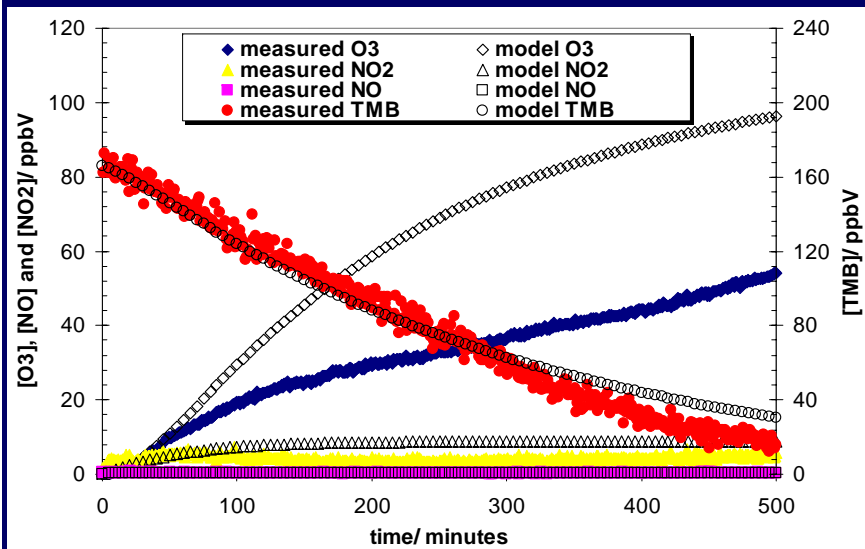
Is this the answer to the reactivity issue?

Measurement = blue, base case simulation = red, tuned mechanism = green, tuned model + constrained with measured NO₂ concentration = orange.

Rickard, Wyche, Metzger et al, PSI chamber, using Leicester CIR-TOF-MS. Comparisons MCM v3.1 vs expt



VOC/NO_x = 2.25

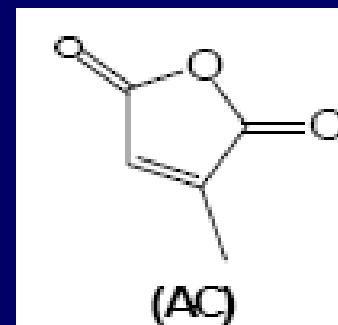
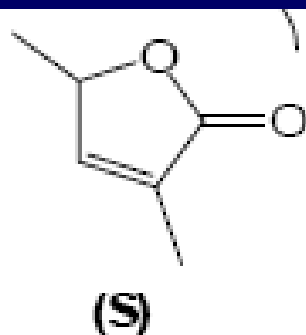
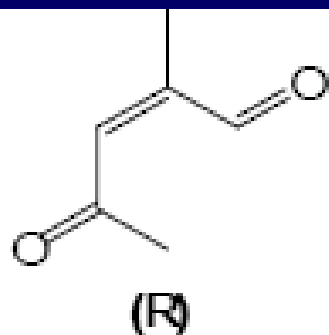
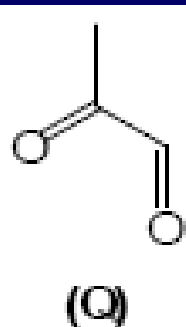


VOC/NO_x = 16.6

- Auxiliary mechanism tuned to PSI chamber and to HONO source
- Model overestimates ozone formation especially at low NO_x
- Good representation of TMB decay, but reactivity underestimated at long times

Model-measurement comparison: Ring opening compounds (1)

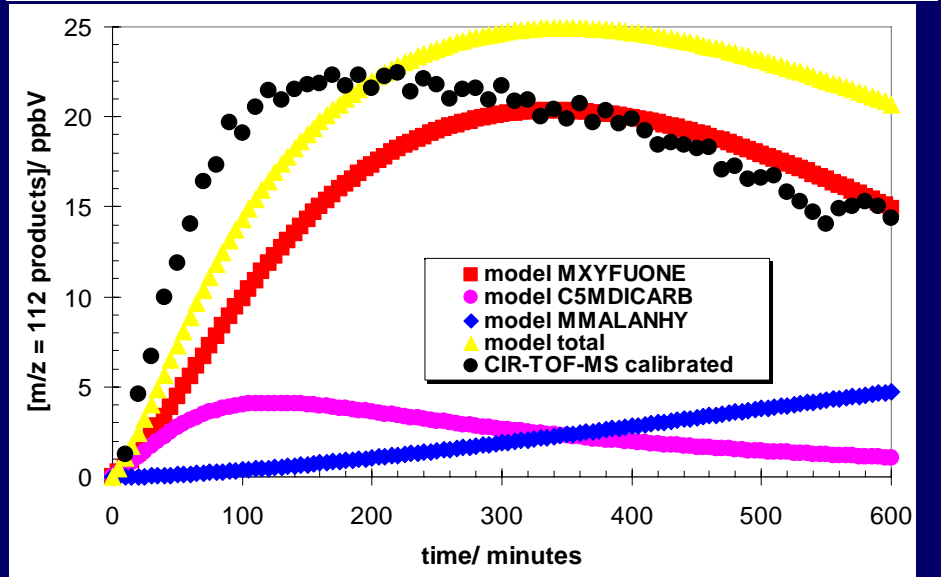
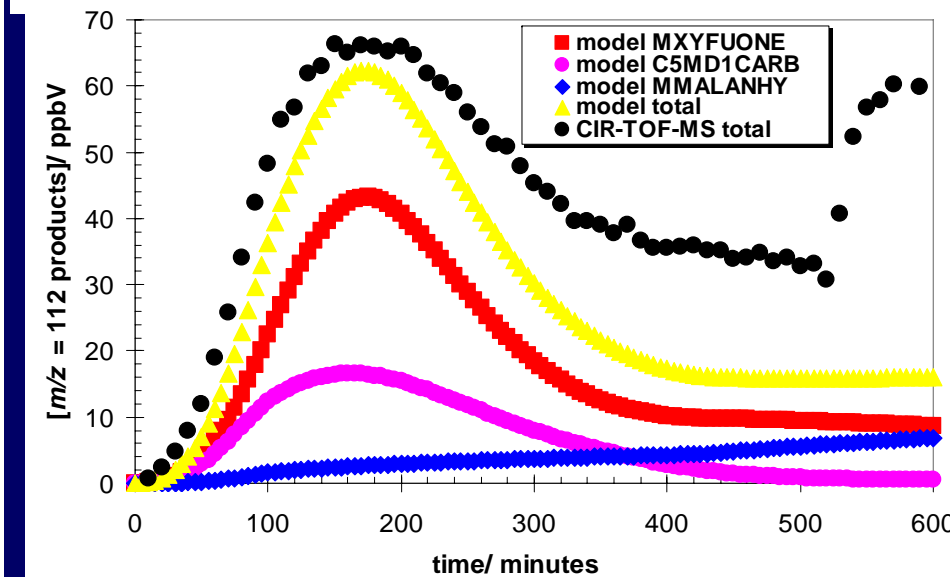
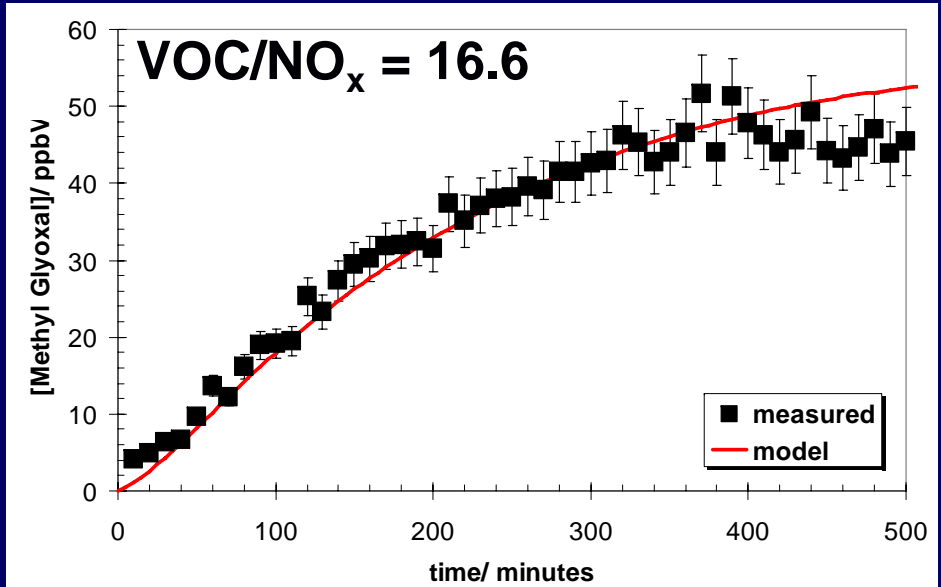
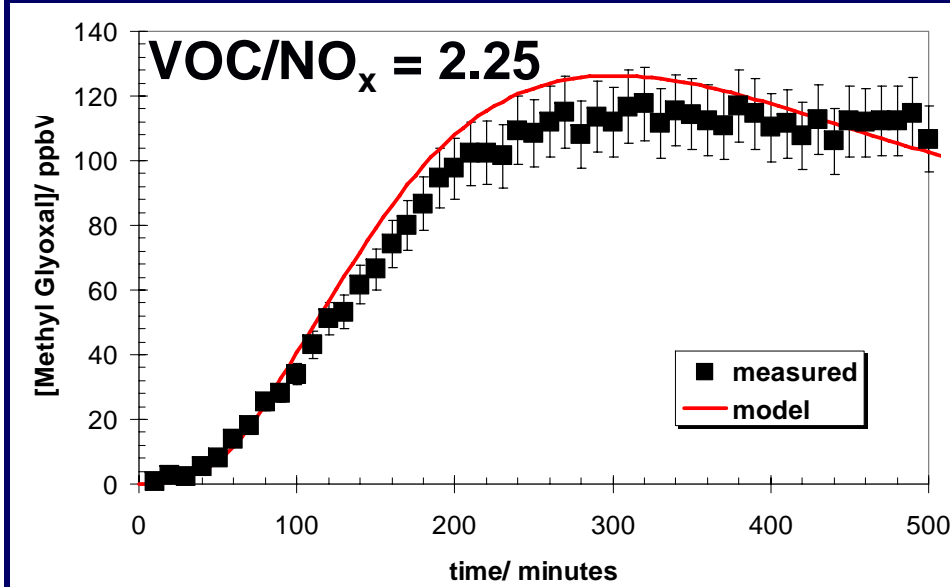
- For TMB, peroxide bicyclic route, according to MCMv3.1, gives methyl glyoxal (Q), the furanone 3,5-dimethyl-5(2H)-2-furanone (S) and the unsaturated γ -dicarbonyl 2-methyl-4-oxo-2-pentanal (R) as co-products.
- Secondary products including citraconic anhydride (3-methyl maleic anhydride, AC) and methyl glyoxal (Q) are produced from the photo-oxidation of the 2-methyl-4-oxo-2-pentanal (R).
- The CIR-TOF-MS signal for $m/z=113$ ($112 + 1$) was taken as a measure of the total ring opening products mentioned above ((R) + (S) + (AC)).



Model-measurement comparison: Ring opening compounds (2)



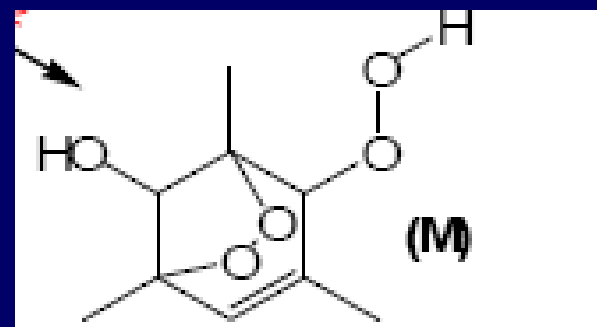
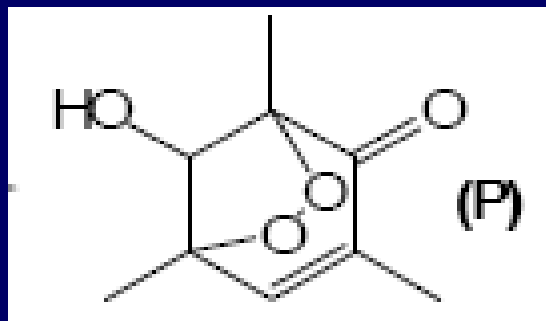
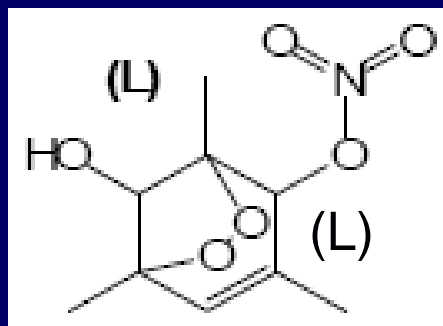
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Rickard et al:

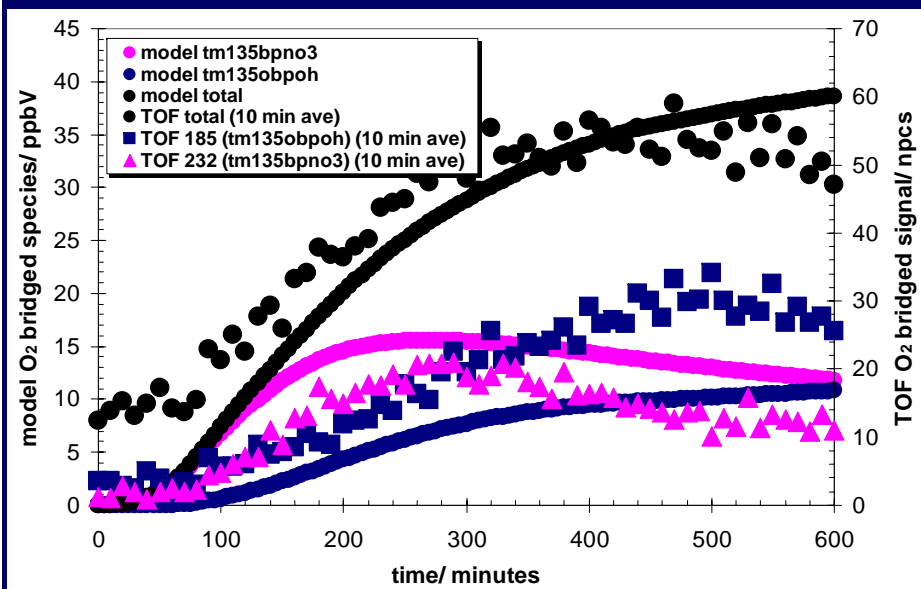
O₂-bridged bicyclic ring retaining products (1)

- In MCMv3.1 peroxide bicyclic ring retaining compounds can be formed e.g. the hydroxy peroxide bicyclic nitrate (L) the hydroxy peroxide bicyclic ketone (P) and the hydroxy peroxide bicyclic peroxide (M):

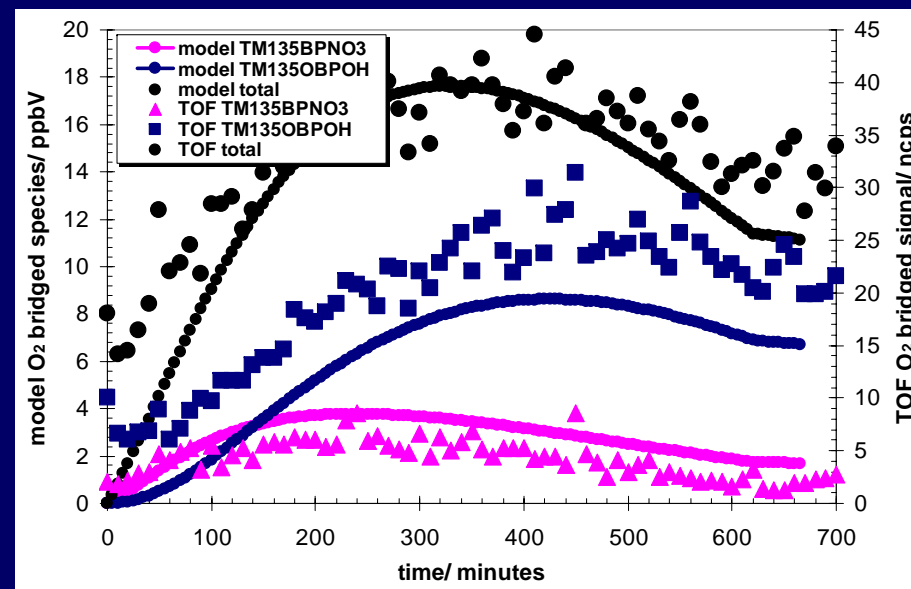


- For both sets of experiments the model-measurement profiles for the hydroxy peroxide bicyclic nitrate ($m/z = 231 + 1$) and ketone ($m/z = 184 + 1$) are in good agreement giving use confidence in the mechanism.

Model-measurement comparison: O₂-bridged bicyclic ring retaining products (2)



VOC/NO_x = 2.25



VOC/NO_x = 16.6

Elena Gomez Alvarez (CEAM) and Jens Hjorth

solid phase microextraction (SPME) using *O*-2,3,4,5,6-(pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) as an in-fibre derivatisation reagent, coupled with analysis of the derivatives using GC/FID

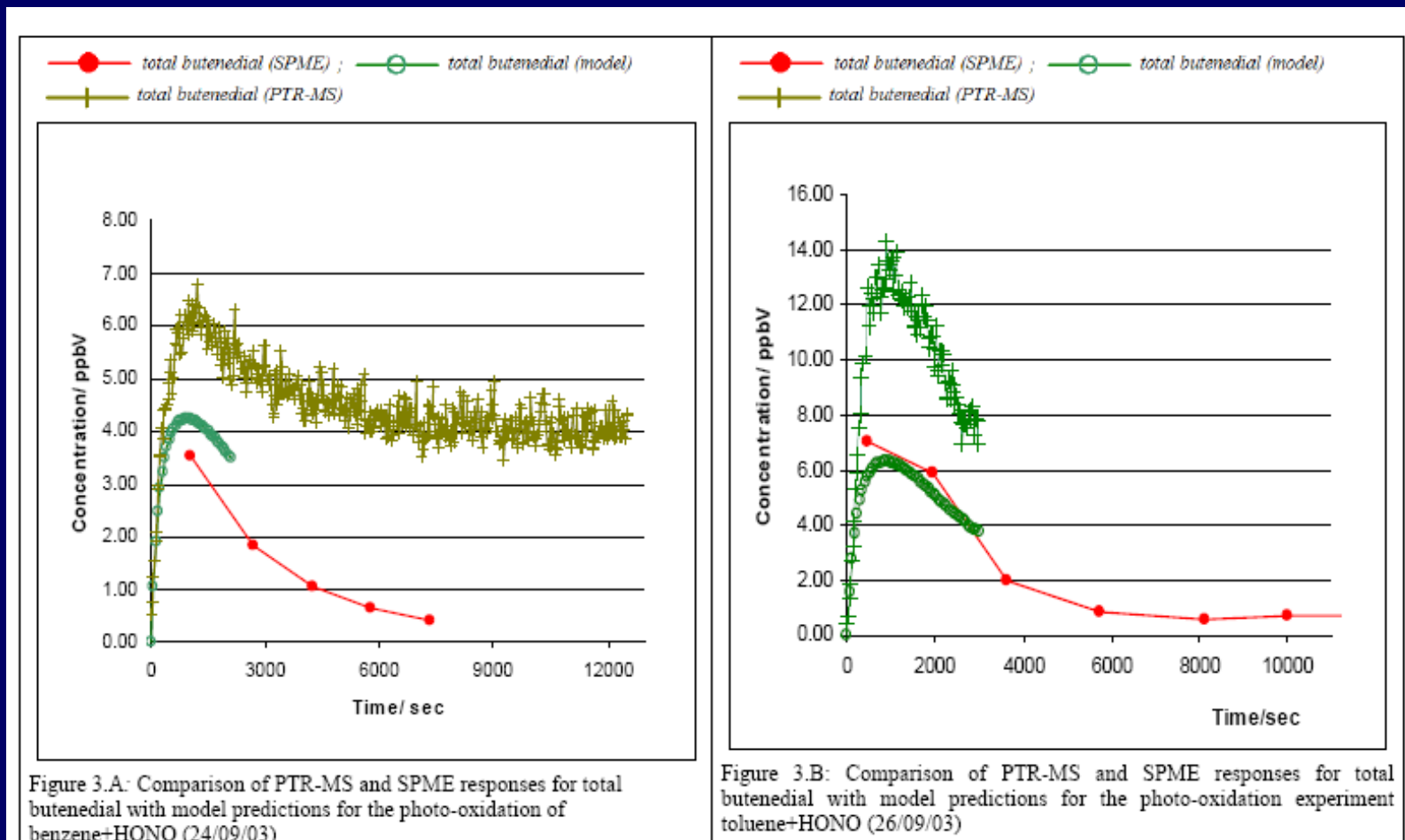


Figure 3.A: Comparison of PTR-MS and SPME responses for total butenedial with model predictions for the photo-oxidation of benzene+HONO (24/09/03)

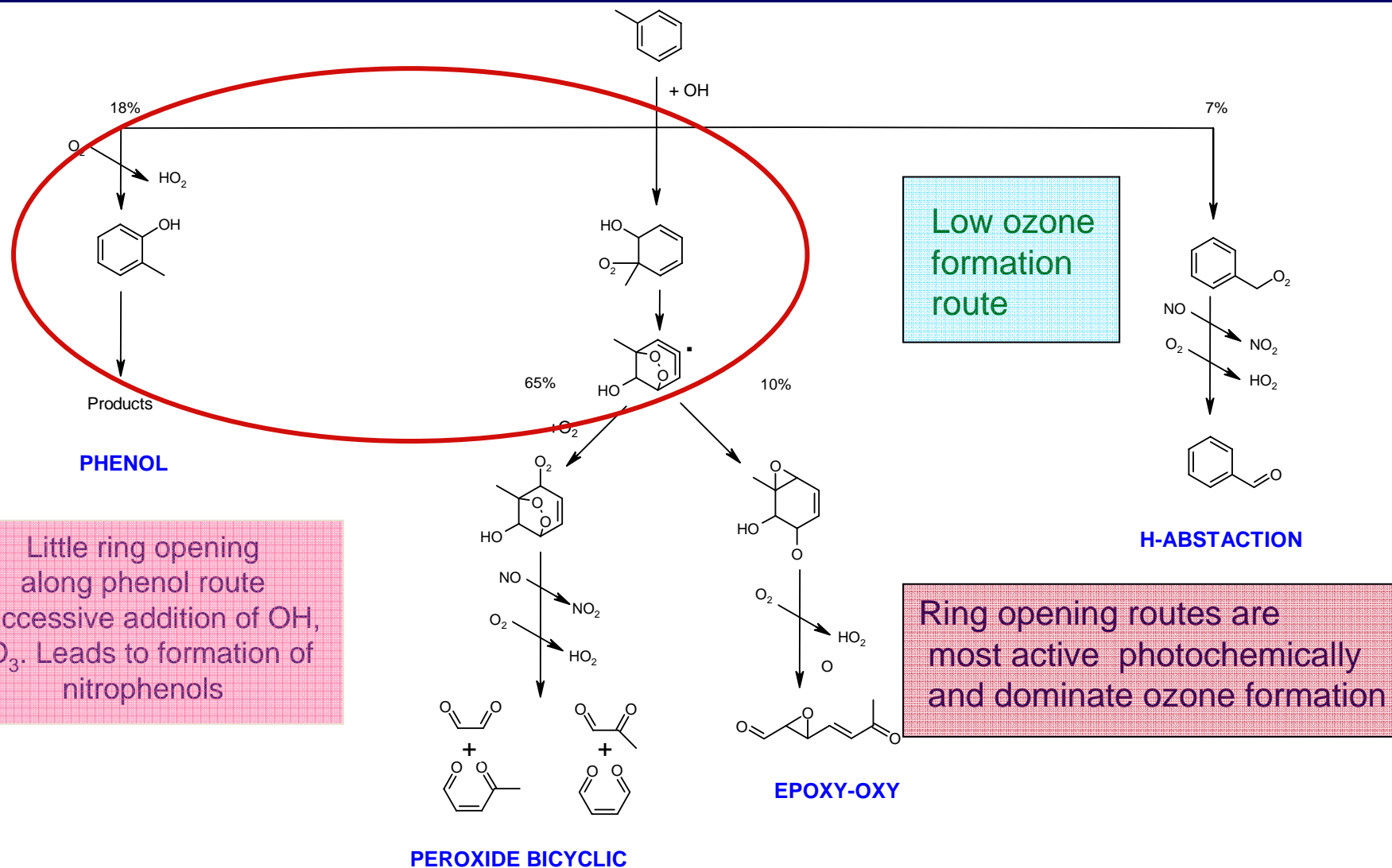
Figure 3.B: Comparison of PTR-MS and SPME responses for total butenedial with model predictions for the photo-oxidation experiment toluene+HONO (26/09/03)

SPME yields vs model yields

<i>Carbonylic product of toluene photo-oxidation</i>	<i>Yield, this work (%)</i>	<i>Yield (%) model</i>	<i>Literature (%)</i>	<i>References</i>
<i>Butenedial CIS</i>	<i>6±3</i>	<i>Not reported</i>	<i>8±3</i>	<i>Berndt and Böge, 2006 (17)</i>
<i>Butenedial TRANS</i>	<i>7±4</i>	<i>Not reported</i>	<i>2.3±0.7</i>	<i>Berndt and Böge, 2006 (17)</i>
<i>Butenedial TOTAL</i>	<i>13±7</i>	<i>12</i>	<i>10,3</i>	<i>Berndt and Böge, 2006 (17)</i>
			<i>Detected</i>	<i>Yu et al, 1997 (15)</i>
<i>Glyoxal</i>	<i>37± 2</i>	<i>35</i>	<i>8-39</i>	<i>Smith et al, 1998 (3)</i>
				<i>Atkinson et al, 1992 (2)</i>
				<i>Volkamer et al, 2001 (8)</i>
				<i>(and references therein)</i>
<i>Methylglyoxal</i>	<i>37± 2</i>	<i>23</i>	<i>7.5-16.7</i>	<i>Smith et al, 1998 (3)</i>
				<i>Atkinson et al, 1992 (2)</i>
<i>2-methylbutenedial</i>	<i><LOD</i>	<i>12</i>	<i>Not reported</i>	<i>Jang and Kamens, 2001 (14)</i>
<i>4-oxo-2-pentenal</i>	<i>>13.8±1.5</i>	<i>12</i>	<i>3,1</i>	<i>Smith et al, 1998 (3)</i>

Gómez Alvarez, E. ; Viidanoja, J.; Muñoz, A.; Wirtz, K.; Hjorth, J. EXPERIMENTAL CONFIRMATION OF THE DICARBONYL ROUTE IN THE PHOTO-OXIDATION OF TOLUENE AND BENZENE. Environ. Sci. Technol. 2007, 41, 8362–8369

Toluene Oxidation Routes in MCMv3.1

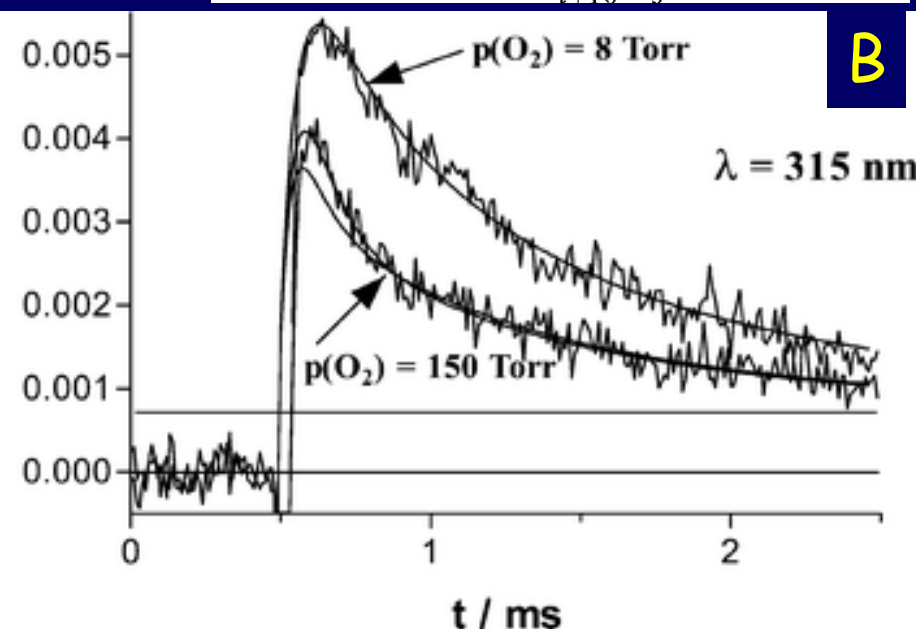
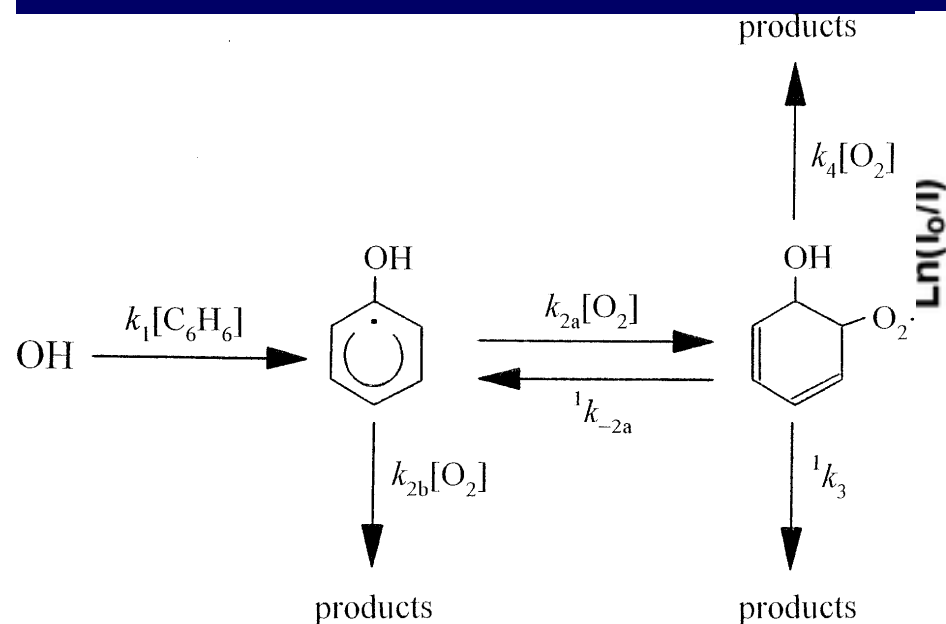
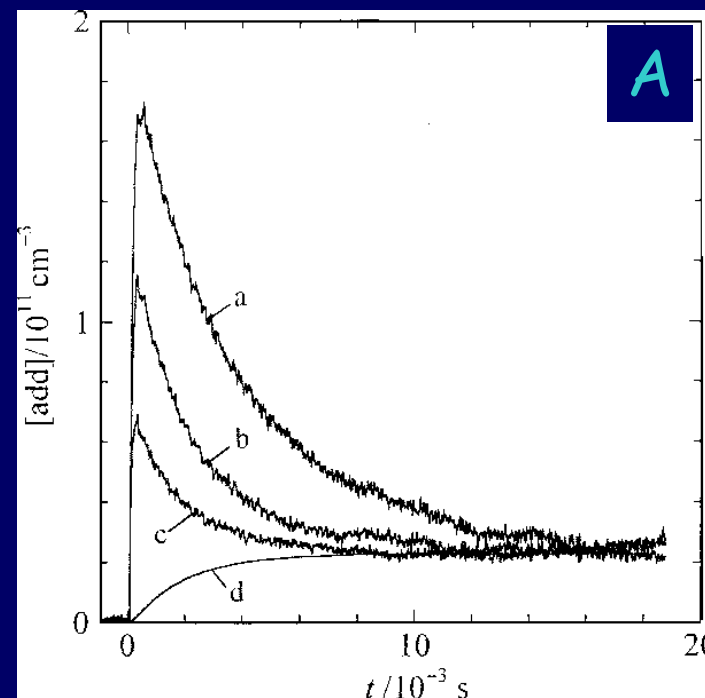


Experimental studies of early chemistry

A Bohn and Zetzsch (PCCP 1999, 1, 5097)
and B Raoult et al (PCCP 2004, 6, 2245)

Flash photolysis studies of the benzene-OH adduct.

Observe equilibration and reactive loss from equilibrated system.

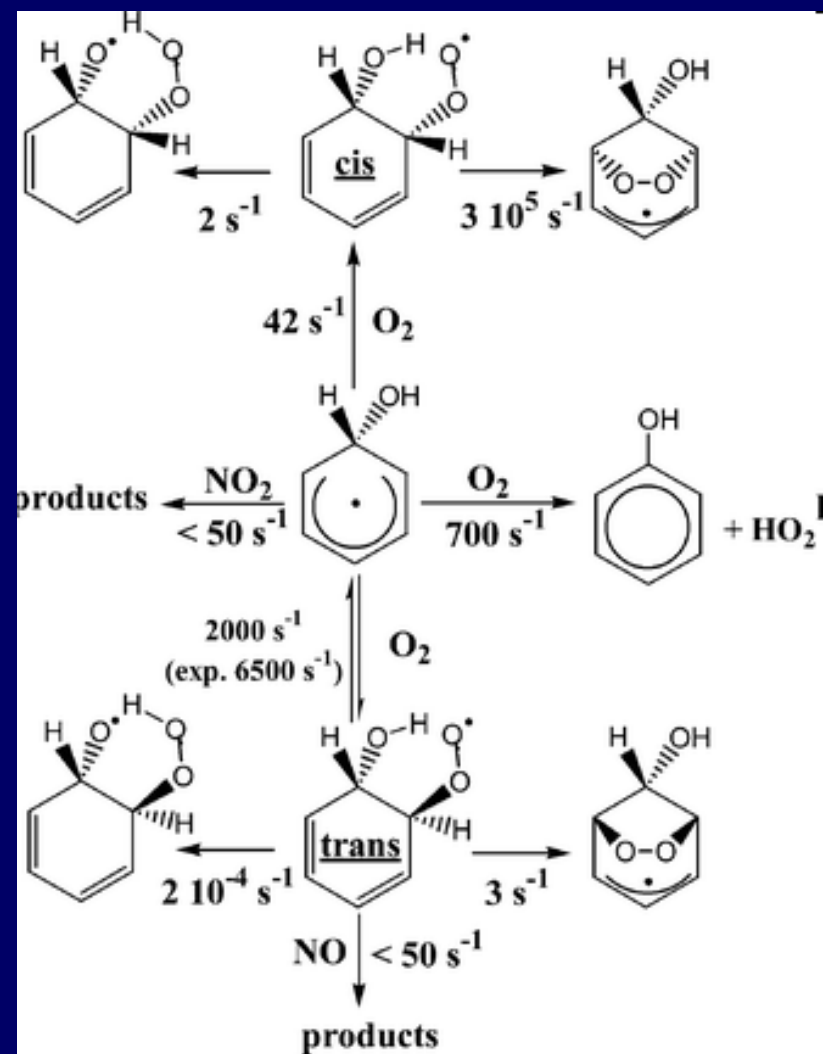


Theoretical studies of early chemistry

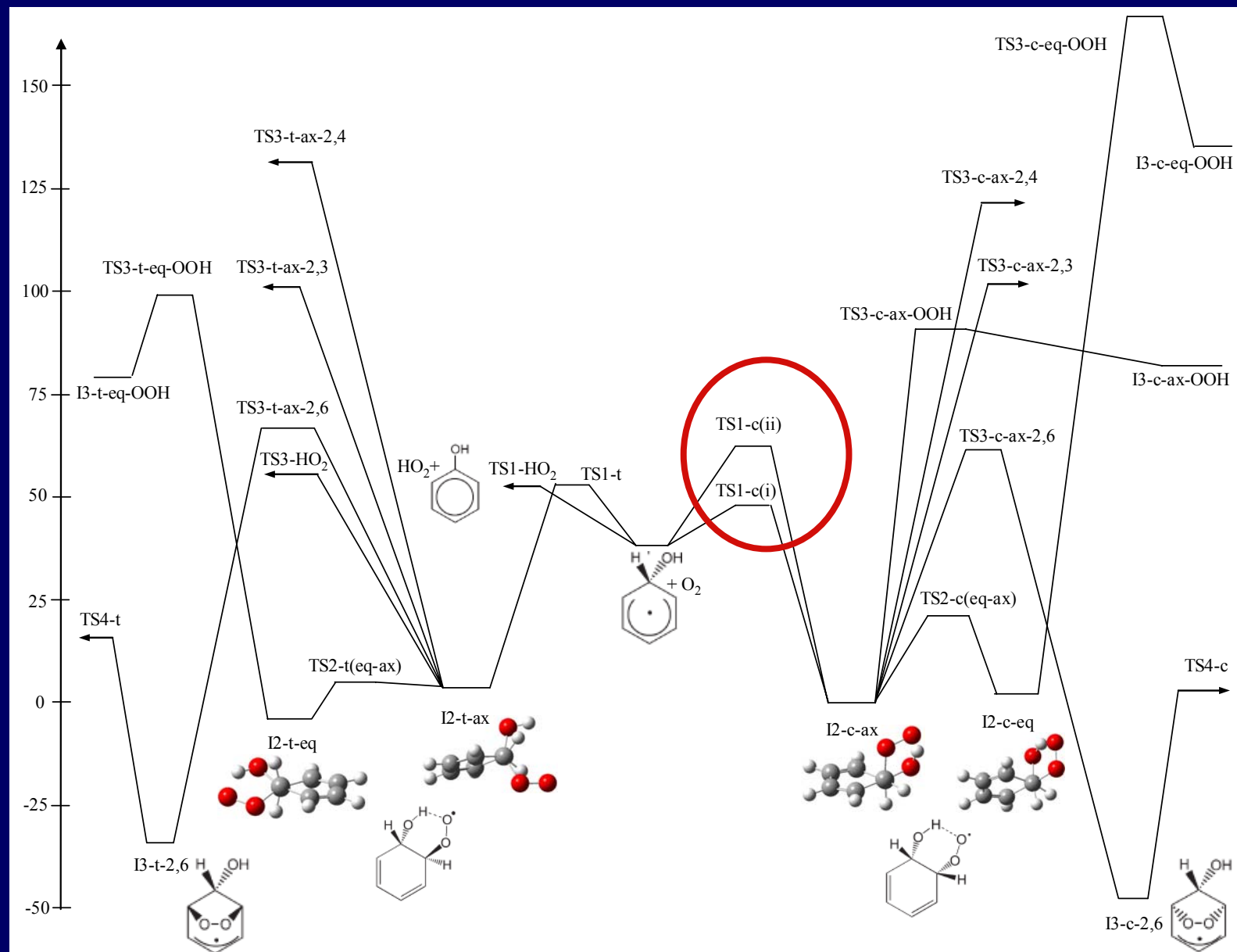
Ghigo and Tonachini (JACS, 1998, 120, 6753; 1999, 121, 836)

Raoult et al (PCCP, 2004, 6, 2245)

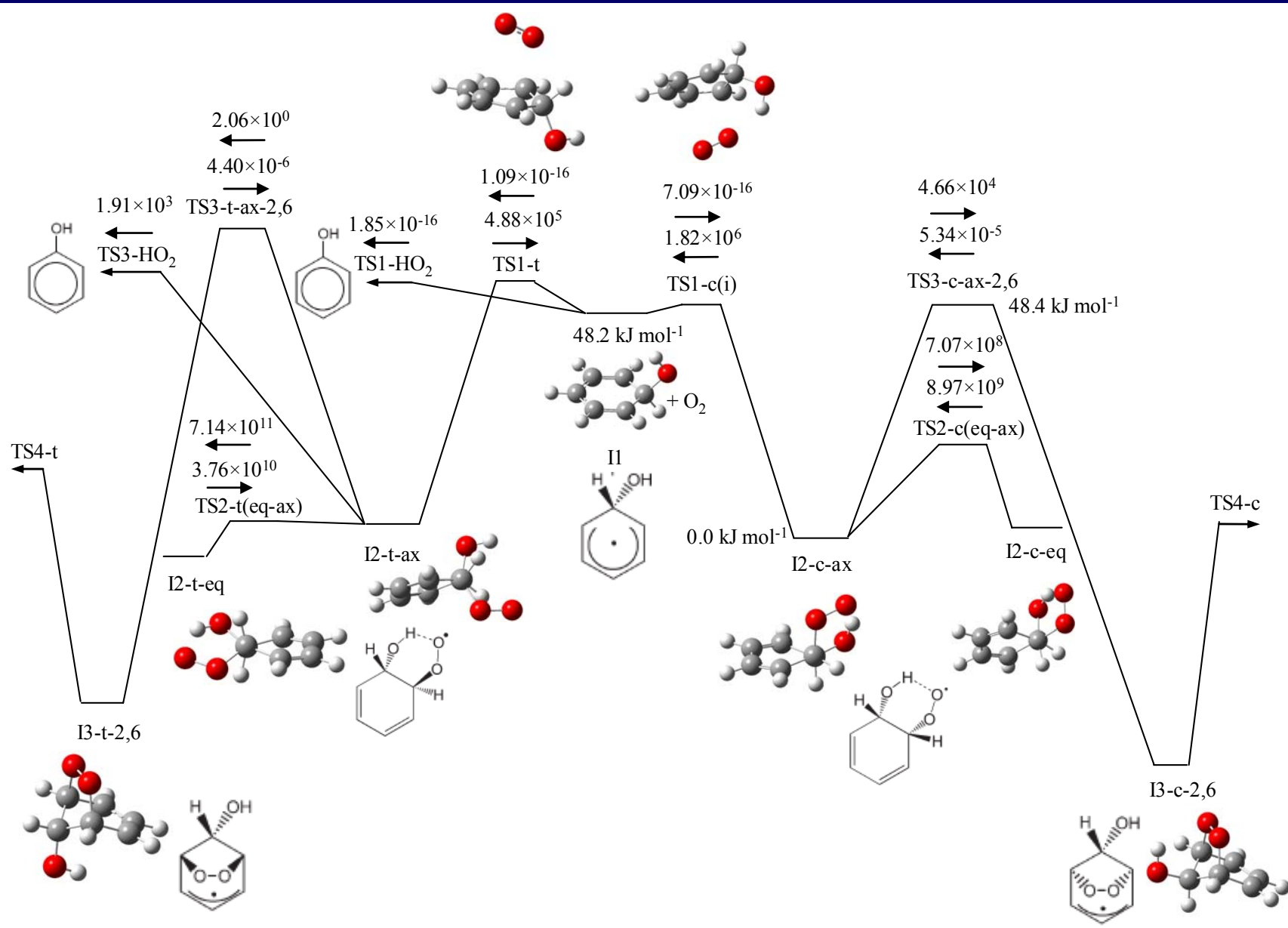
For benzene, addition forms cis and trans ortho O_2 adducts, but route to bicyclic compound is too slow.



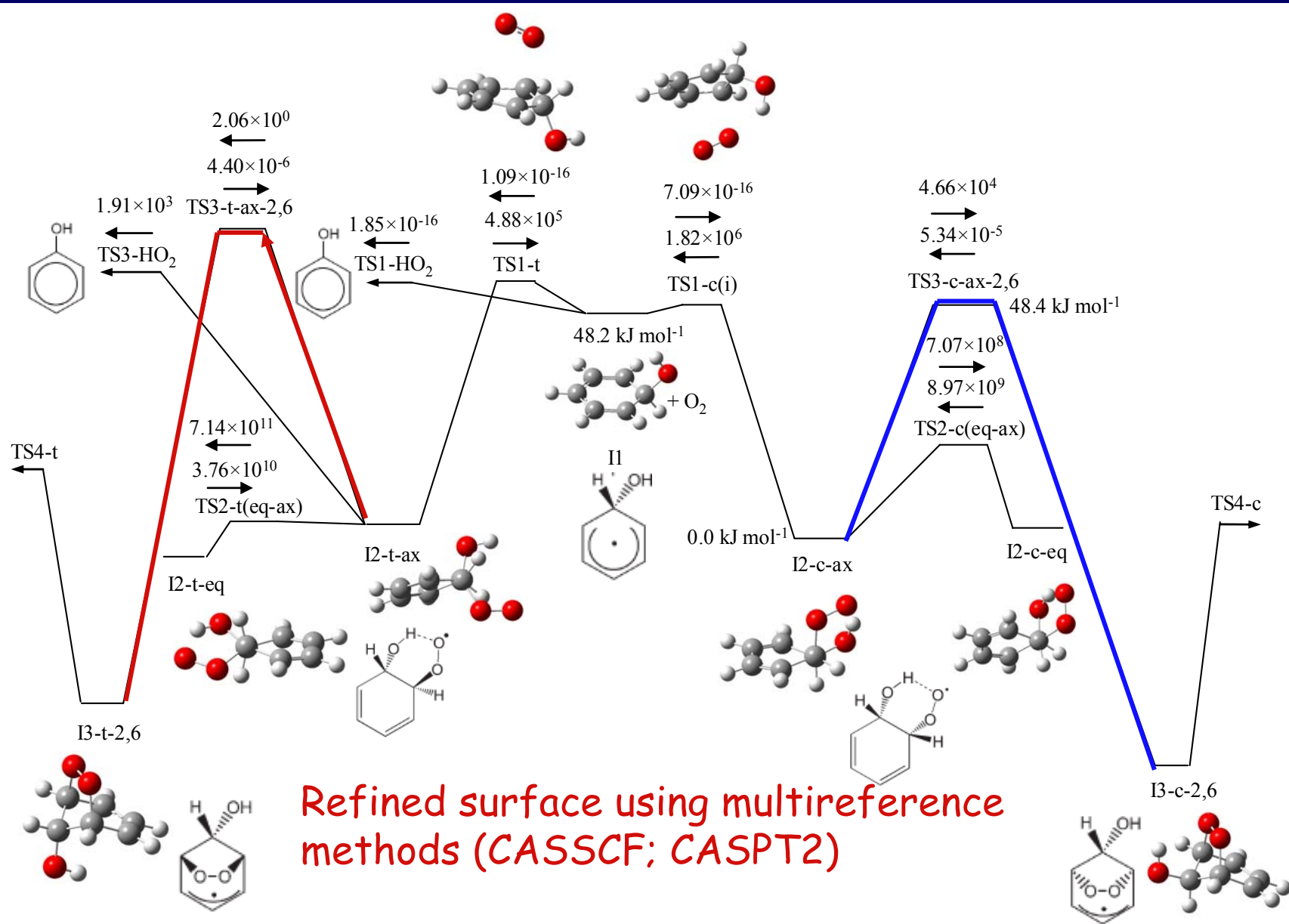
David Glowacki (Leeds) - G3X(MP2)-RAD potential energy surface



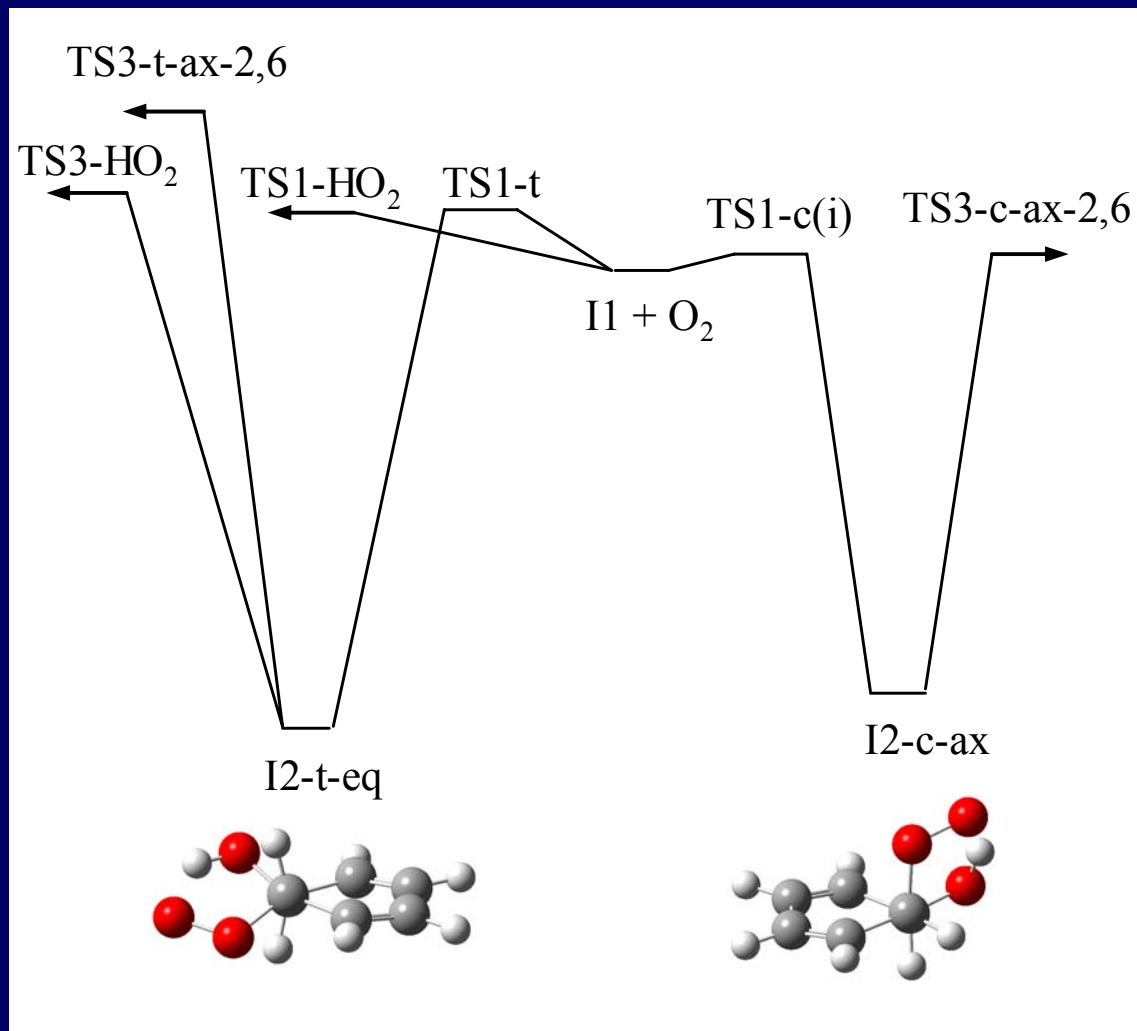
Main features of G3X(MP2)-RAD potential energy surface



Main features of G3X(MP2)-RAD potential energy surface

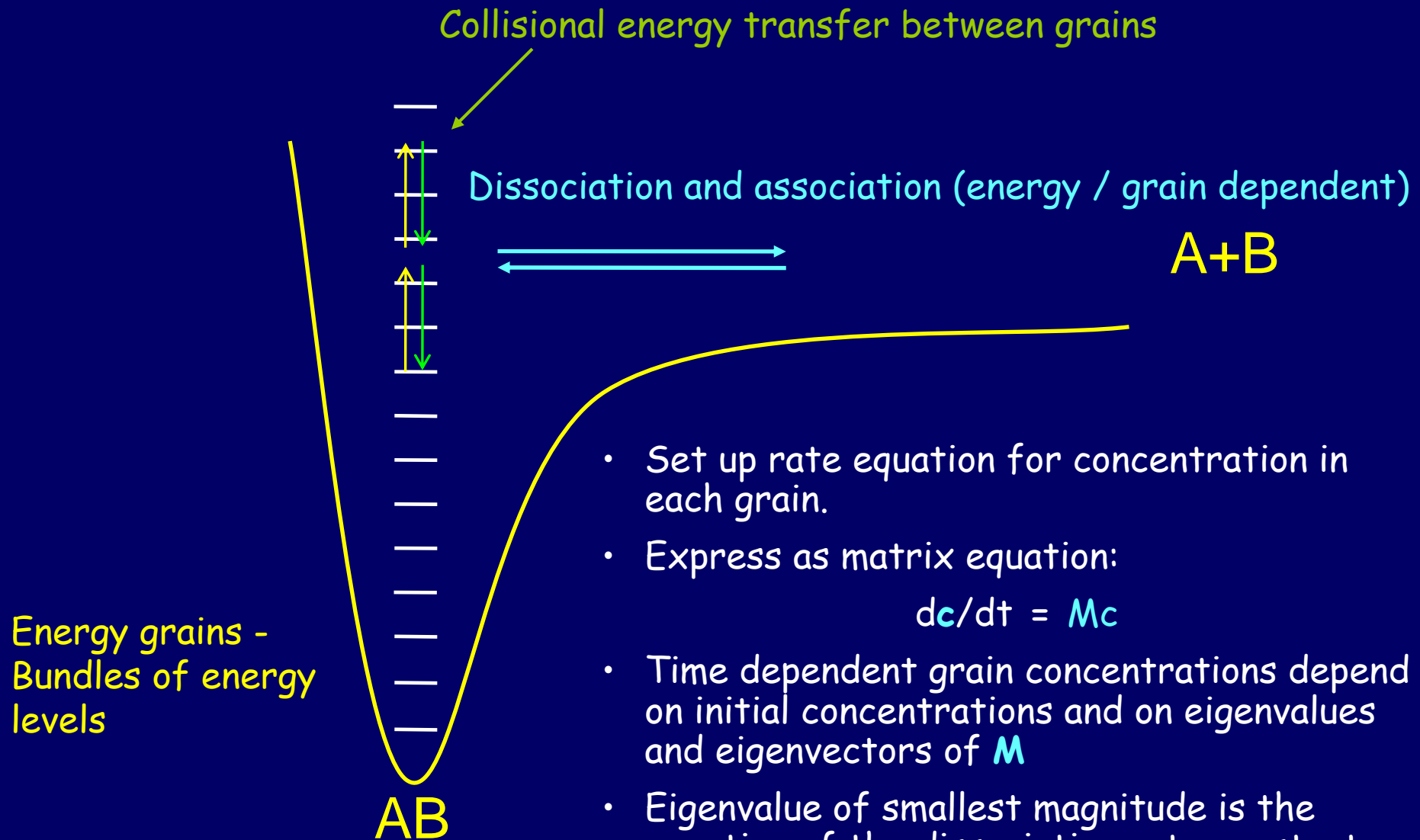


Skeleton potential energy surface for use with master equation calculations



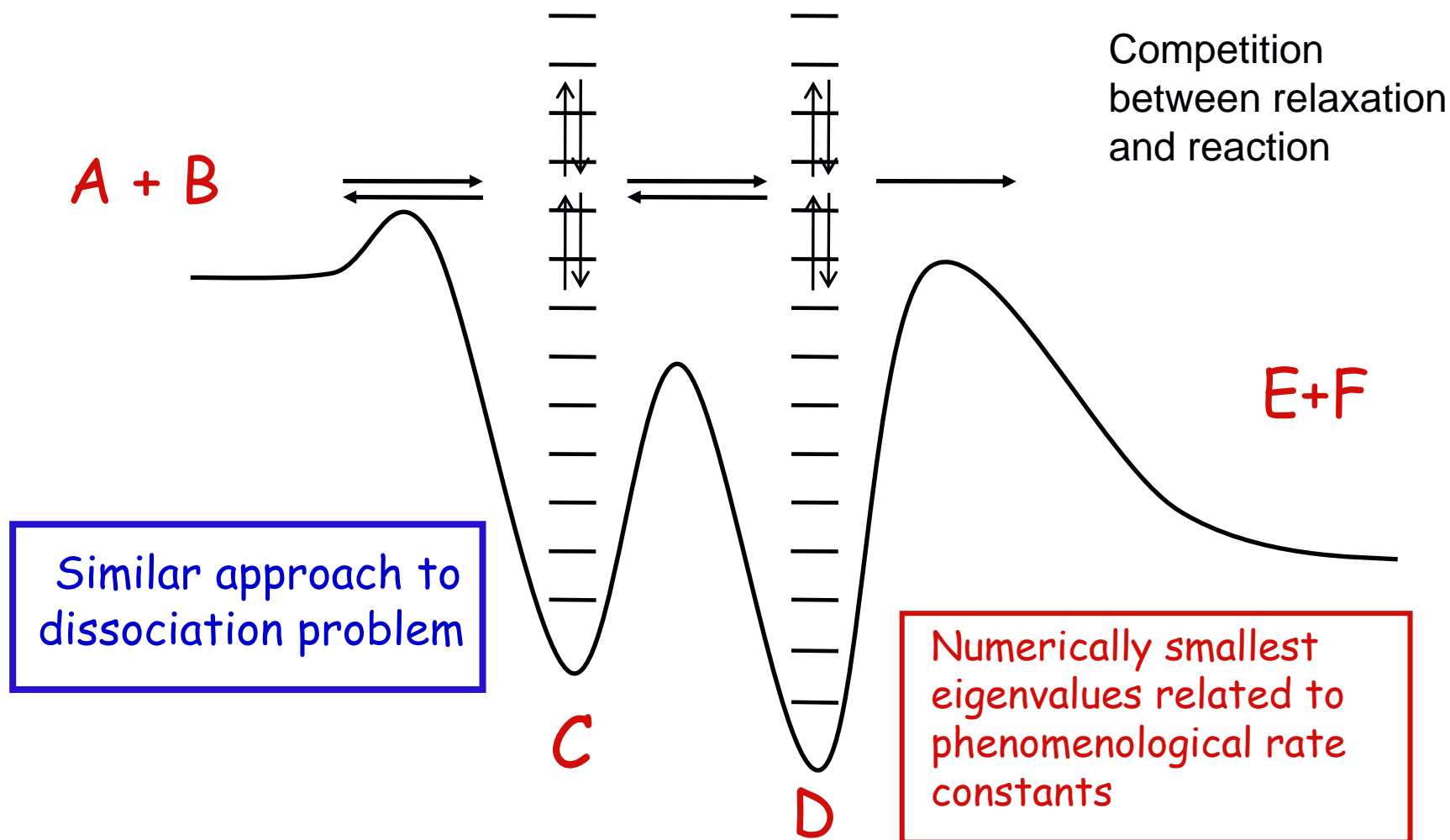
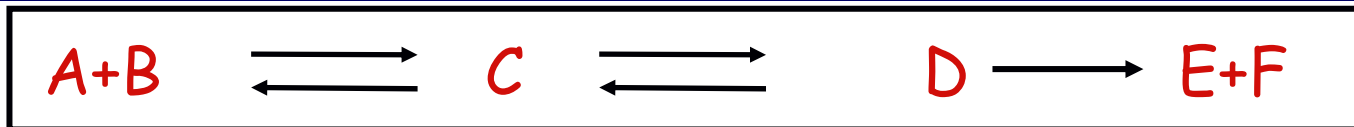
How do we accommodate the pressure dependence in models?

Modelling dissociation and association reactions - master equation analysis



- Set up rate equation for concentration in each grain.
- Express as matrix equation:
$$dc/dt = Mc$$
- Time dependent grain concentrations depend on initial concentrations and on eigenvalues and eigenvectors of M
- Eigenvalue of smallest magnitude is the negative of the dissociation rate constant.

More complex reactions.



Kinetics experiments vs theory

Experiment



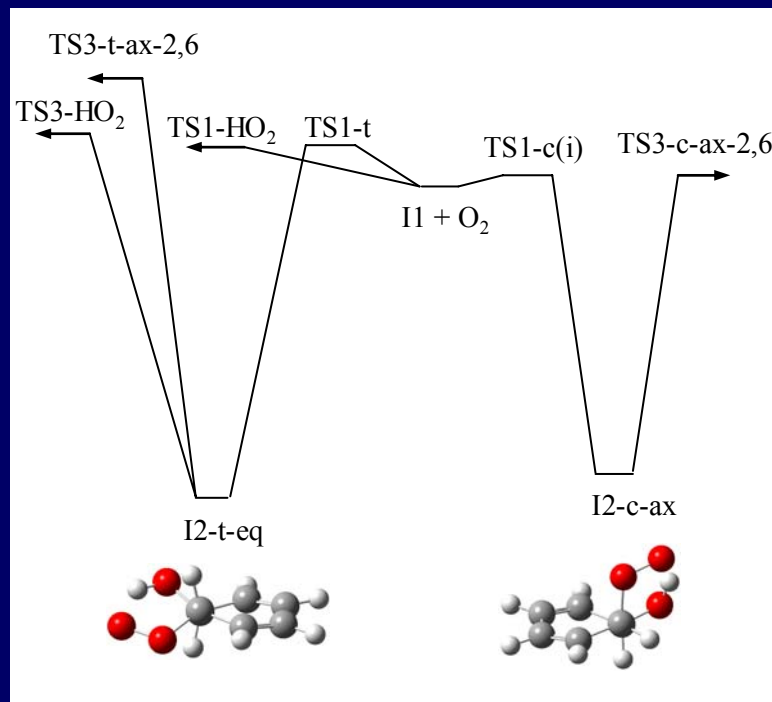
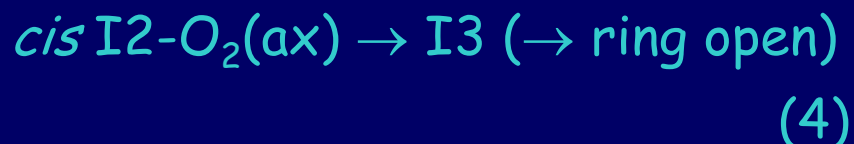
Raoult et al (Also Zetzsch and group) Observation of I1



Experiment shows equilibration and loss of species from equilibrium (biexponential decay)

Analysis gives k_1 , k_{-1} and k_2 .
Reaction 2 corresponds to routes leading to phenol and to ring opening

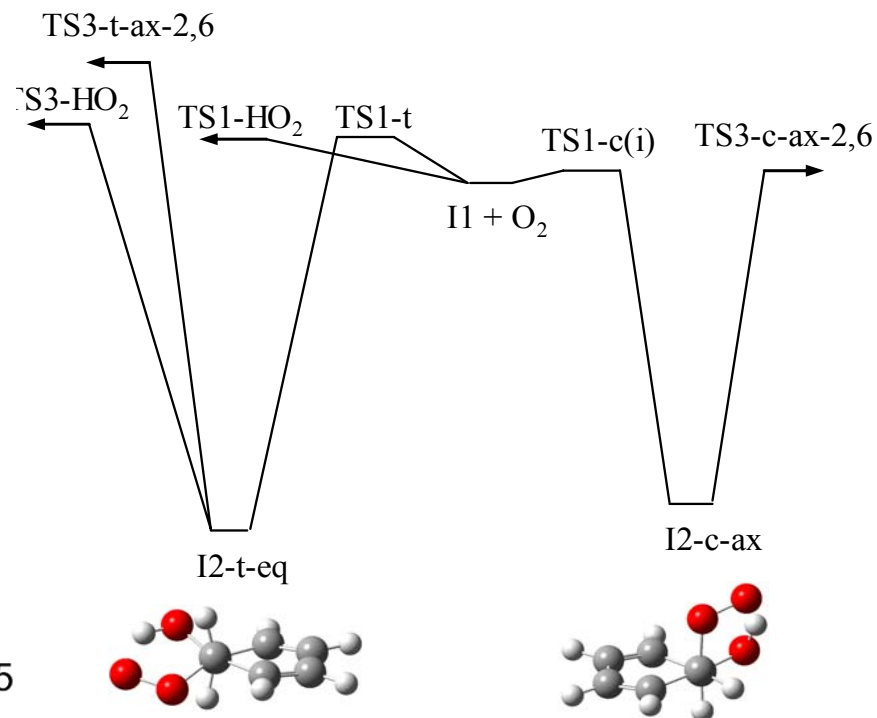
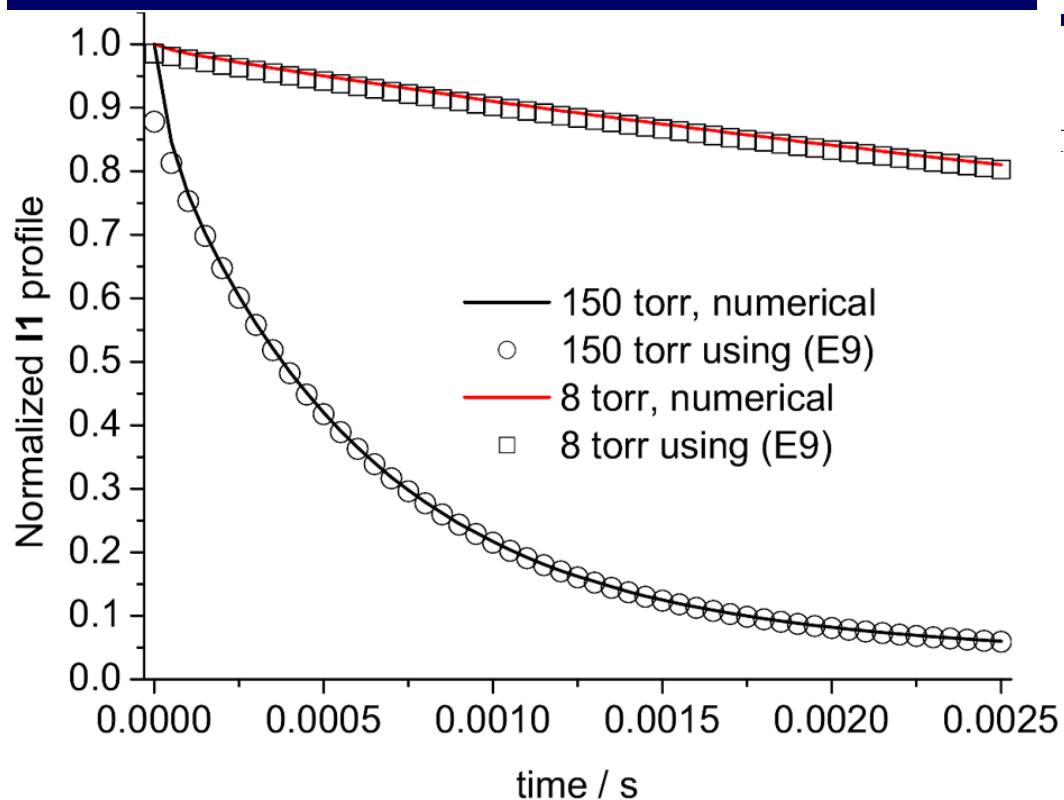
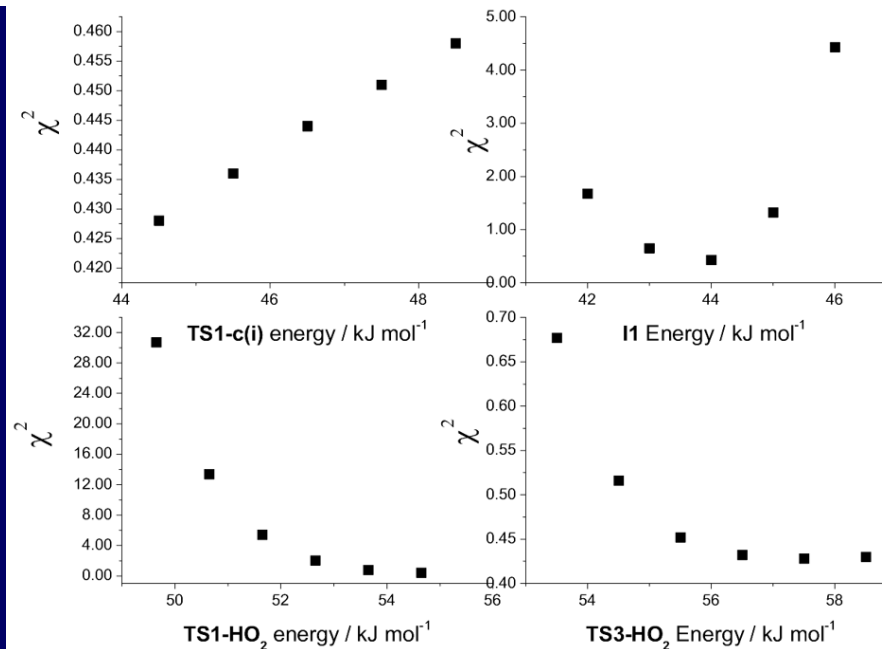
Theory



Fitting model to experiment

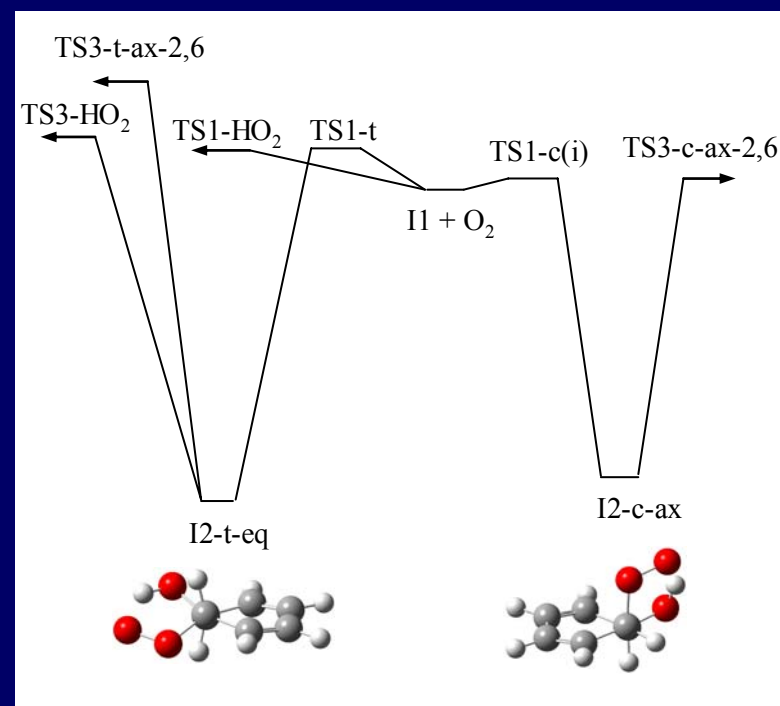
PES / master equation gives
3 chemical eigenvalues.

Vary 4 energies and fit to 2
experimental eigenvalues



Current results

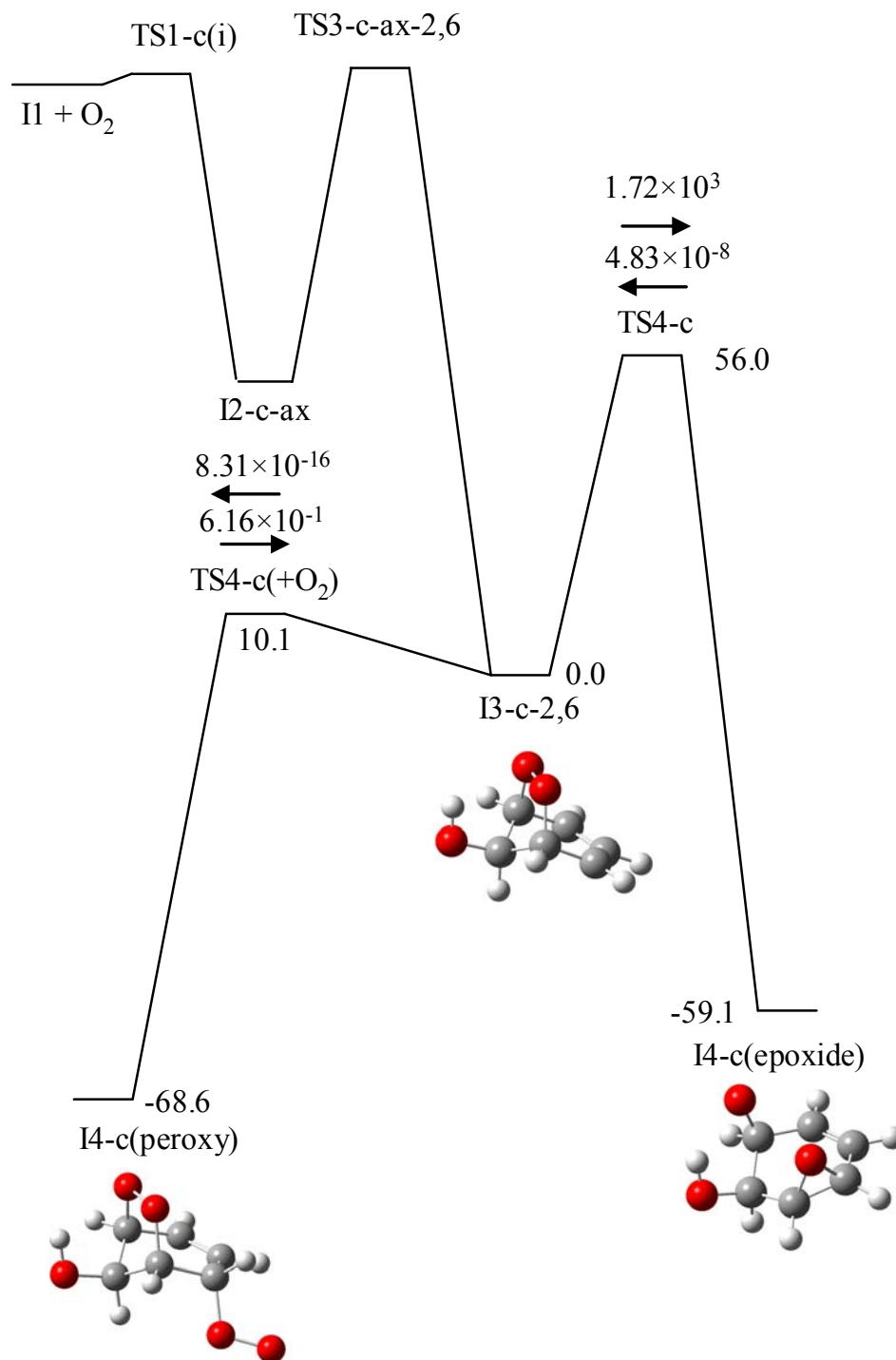
Reaction	Rate Coefficient
$\text{I1} + \text{O}_2 \rightarrow \text{I2-c-ax}$	2.78×10^{-15}
$\text{I2-c-ax} \rightarrow \text{I1} + \text{O}_2$	9.76×10^4
$\text{I1} + \text{O}_2 \rightarrow \text{I2-t-eq}$	1.01×10^{-15}
$\text{I2-t-eq} \rightarrow \text{I1} + \text{O}_2$	4.93×10^3
$\text{I1} + \text{O}_2 \rightarrow \text{TS1-HO}_2$	1.56×10^{-16}
$\text{I2-c-ax} \rightarrow \text{TS-c-ax-2,6}$	3.06×10^3
$\text{I2-t-eq} \rightarrow \text{TS3-HO}_2$	1.47×10^2



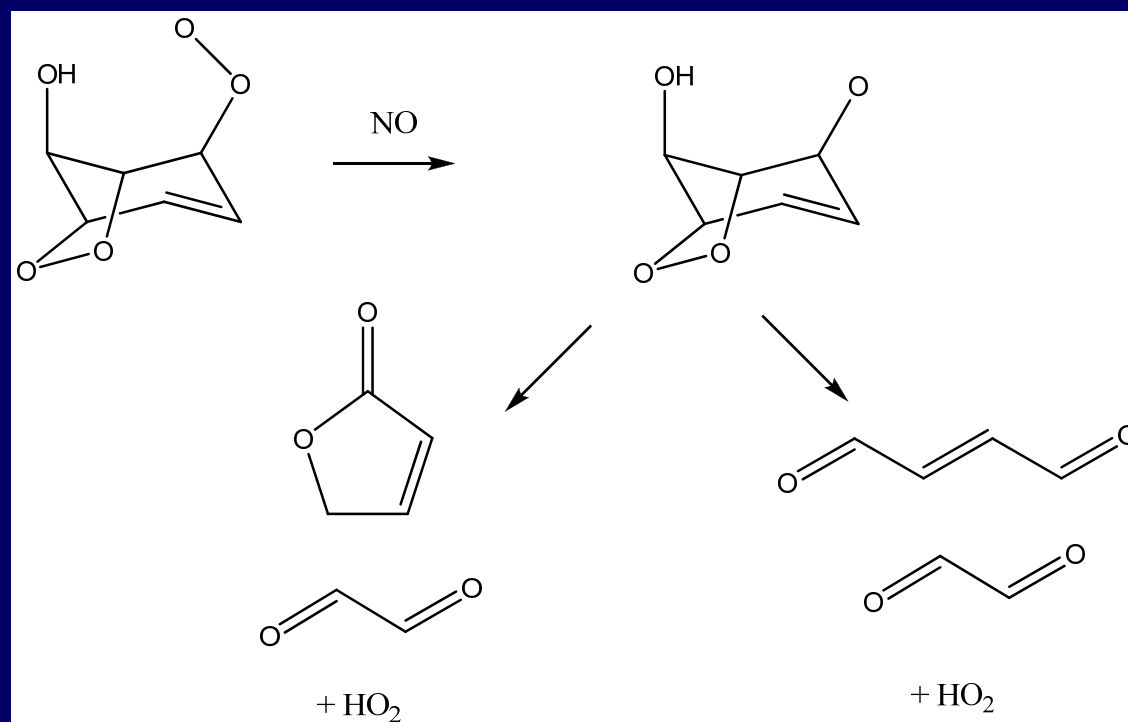
BUT.....

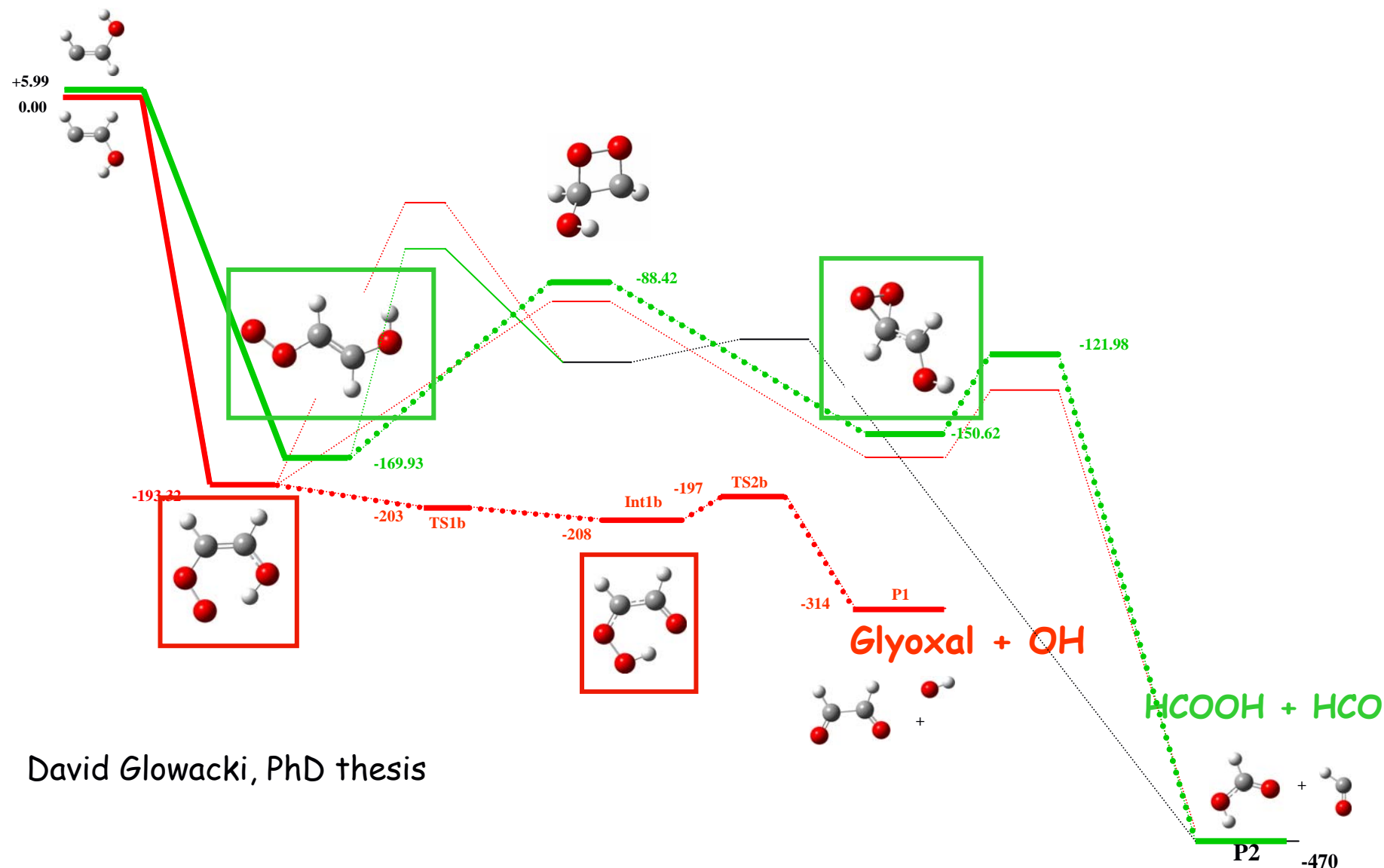
Subsequent chemistry in ring opening channel.

- Calculations support established mechanism involving formation of a bridged peroxy (I3-c-2,6)
- I3 can add a further O_2 or isomerise to form an epoxide.
- The calculations show that the reactions are competitive under atmos conditions, but significant uncertainty in TS energies.



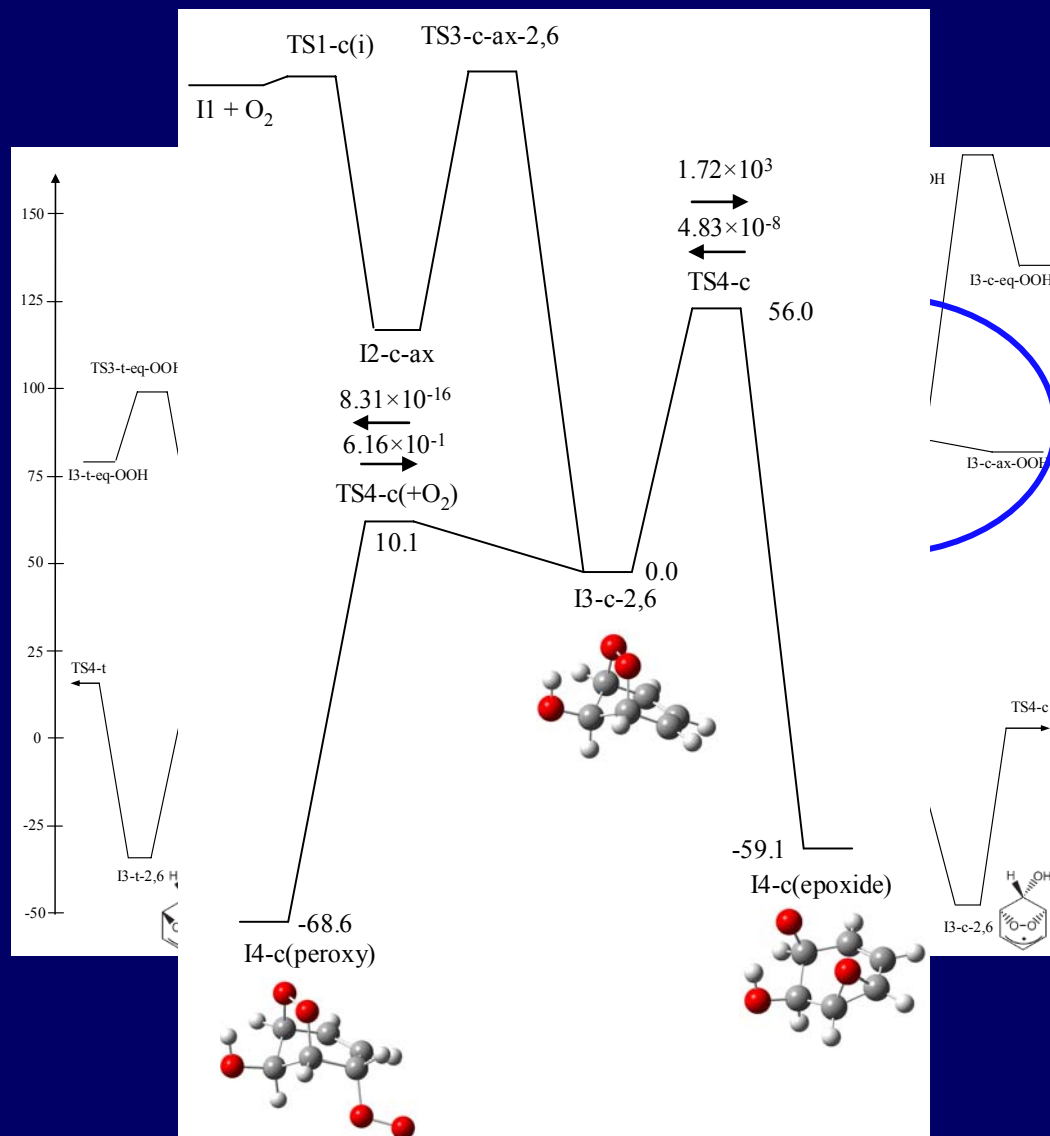
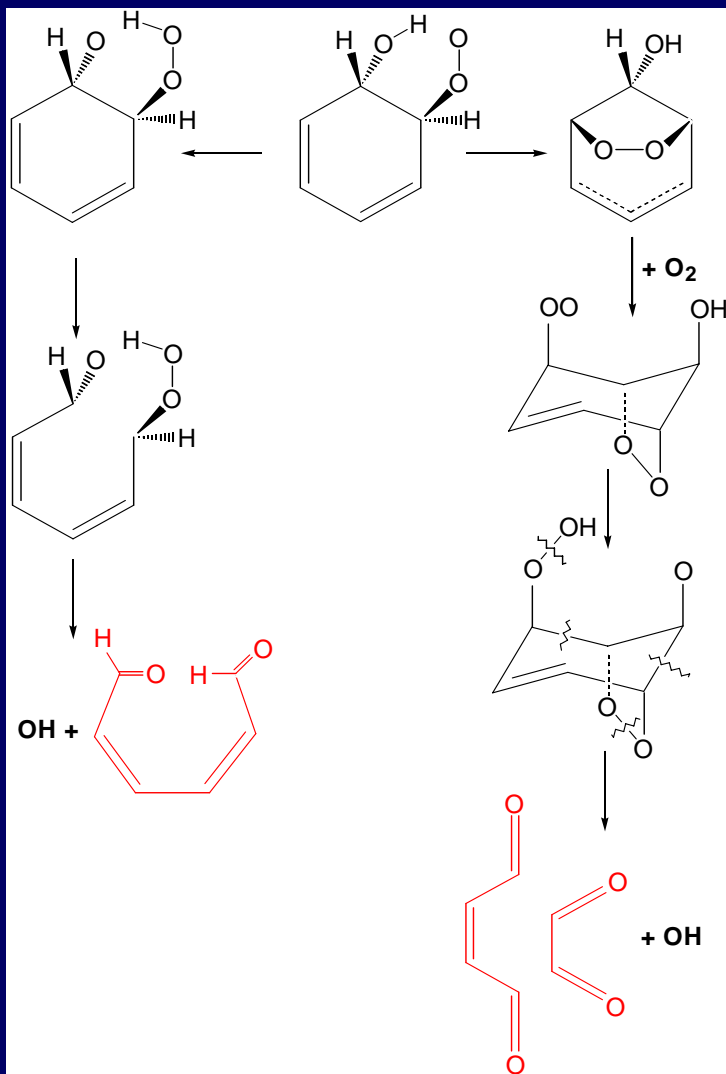
MCM - ring opening reactions





David Glowacki, PhD thesis

Isomerisation routes to OH - Mike Jenkin



Where do we go from here?

- Calculations only mean something when they are used in conjunction with experiments:
 - Use available experimental data to tune surface.
 - Design new experiments - use cavity ring down in laser flash photolysis, with variable T and p to test mechanism more fully
 - Campaign at EUPHORE on toluene (EUROCHAMP2). Highly instrumented. Design expts using MCM, existing results, and ab initio / master equation.
 - Need experiments on an intermediate timescale (~ seconds to minutes). How?
- Extend:
 - Reactions of bicyclic peroxy ? Isomerisation to give OH?
 - PES calculations on toluene (Baoshan Wang)
- New code available soon (Leeds and CEAM) to simulate experiments and test MCM (EUROCHAMP 1,2).

Acknowledgements

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Claire Bloss

Dave Glowacki

Andrew Rickard

EXACT consortium - especially Ian Barnes

EUROCHAMP