SAND2011-4726C

Pressure dependent OH yields in alkene + HO_2 reactions: A theoretical study

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July 10-14, 2011
MIT, Cambridge, MA
The 7th International Conference on Chemical Kinetics

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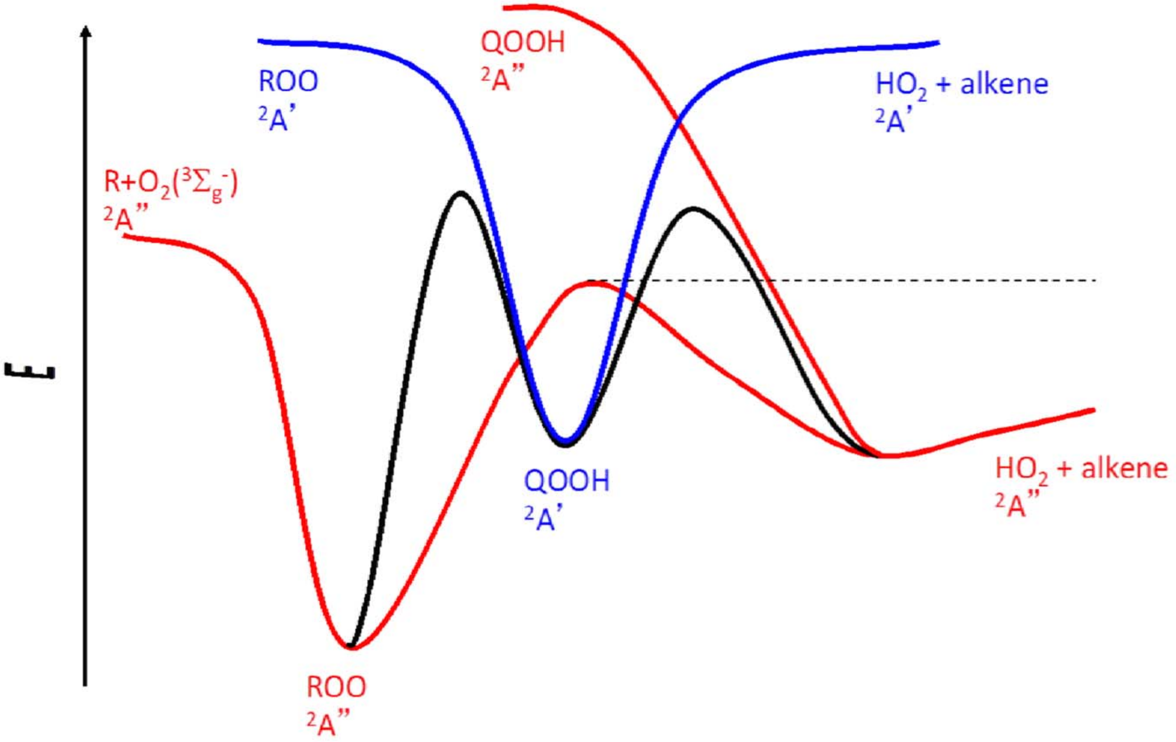
Recap of the alkyl + O_2 story

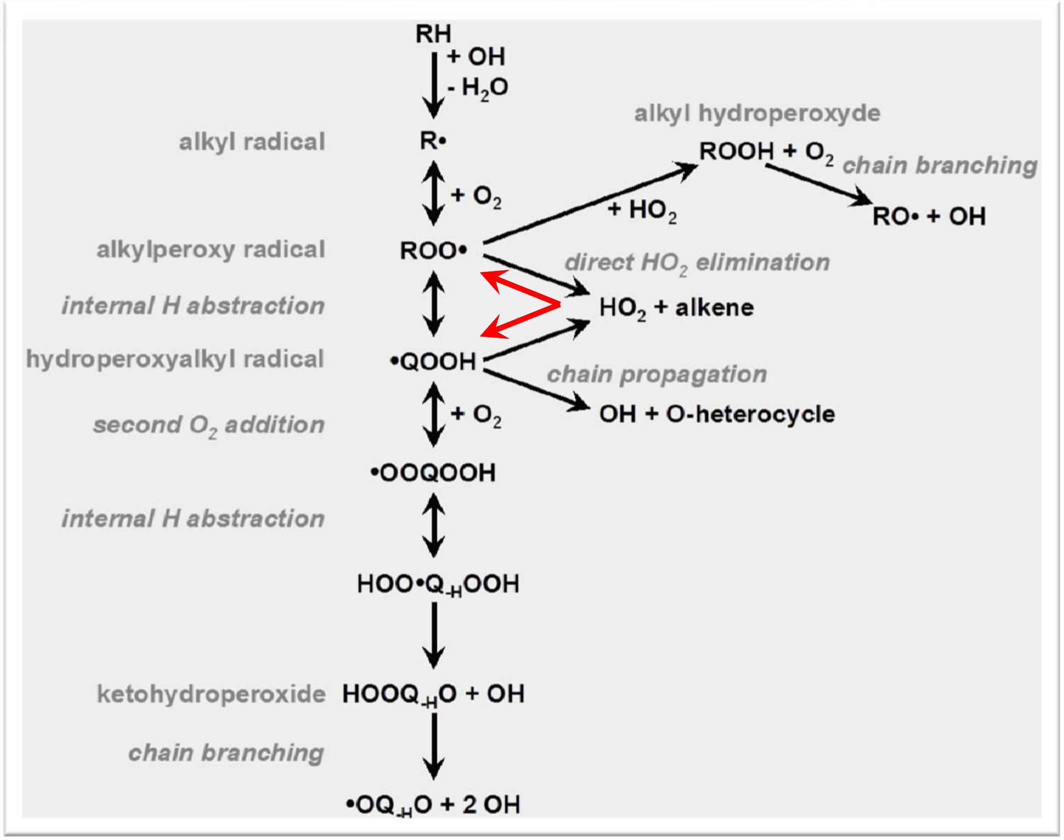
HO_2 formation: $R^{\bullet} + O_2 \rightarrow$ alkene + HO_2

However: alkene + $HO_2 \rightarrow {}^{\bullet}QOOH \rightarrow$ oxirane + OH



In the forward direction the problem has been reconciled by the direct HO_2 elimination pathway, but what about the reverse direction?

The alkene + HO_2 reaction is a potentially crucial reaction at low *T* and high P.



RH

+ OH

- H_2O

alkyl radical R•

+ O_2

alkylperoxy radical ROO•

internal H abstraction

hydroperoxyalkyl radical •QOOH

second O_2 addition

+ O_2

•OOQOOH

internal H abstraction

$HOO{\bullet}Q_{-H}OOH$

ketohydroperoxide $HOOQ_{-H}O$ + OH

chain branching

$\bullet OQ_{-H}O$ + 2 OH

+ HO_2

alkyl hydroperoxyde

ROOH + O_2

chain branching

RO• + OH

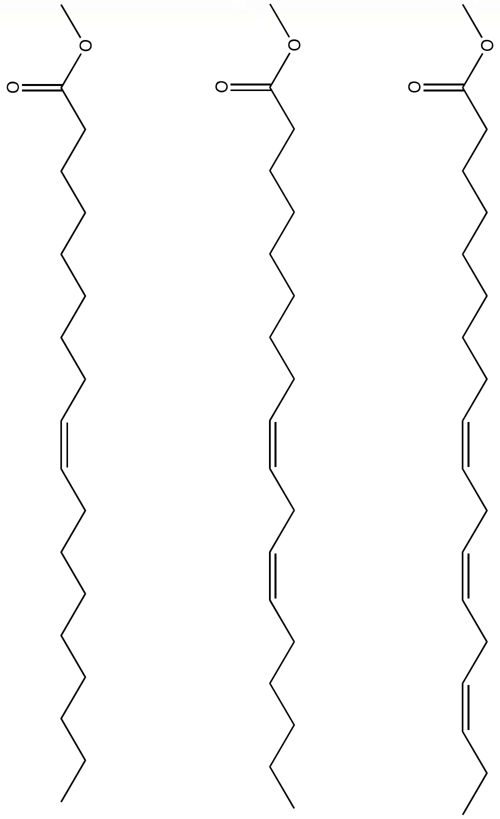
direct HO_2 elimination

HO_2 + alkene

chain propagation

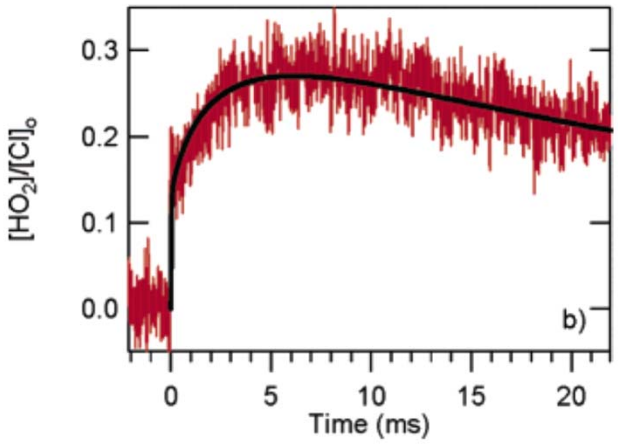
OH + O-heterocycle

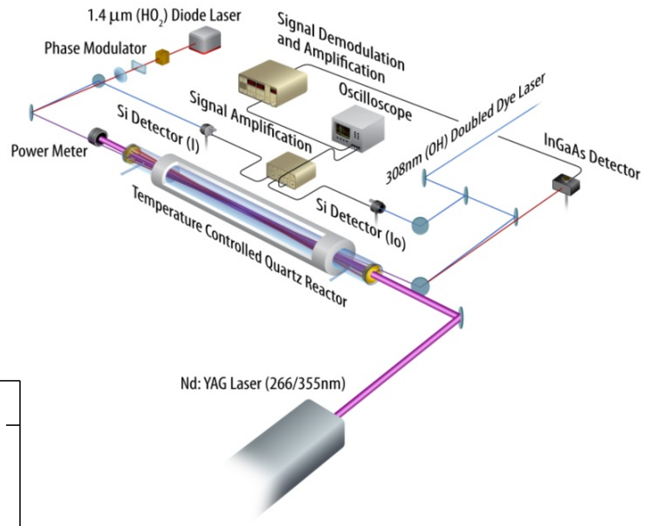
The alkene + HO_2 reaction can influence the reaction flow leading to autoignition.

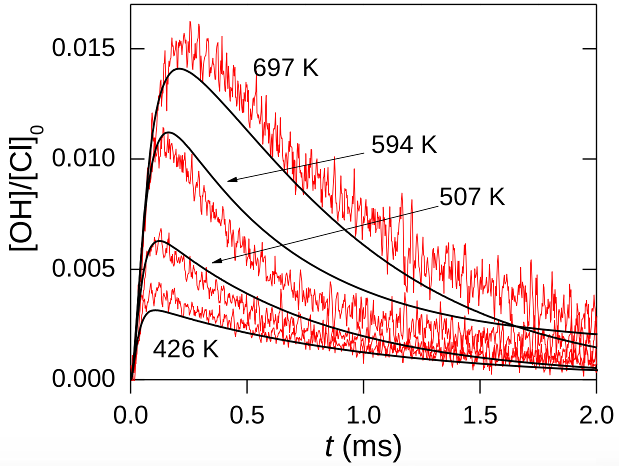


From the most common five methyl esters found in canola or rapeseed oil, three contain double bonds.

HO_2 and OH production from alkyl + O_2 reactions were successfully probed in previous studies.





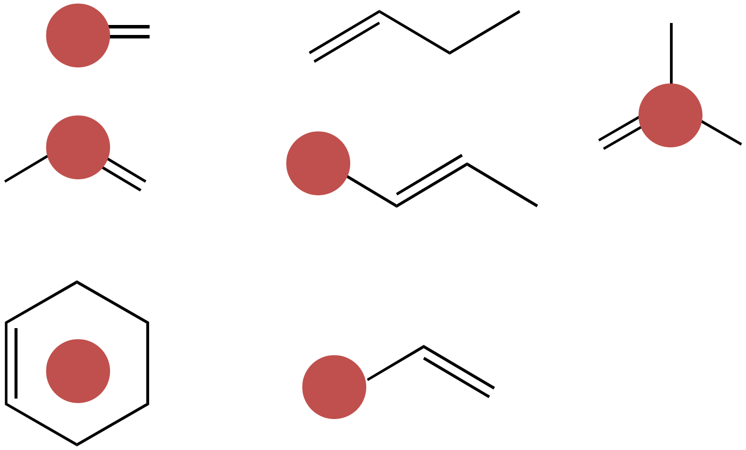


Taatjes lab @ CRF

Time-resolved experiments coupled with rigorous master equation calculations were able to describe time-dependent OH and HO_2 profiles in a wide *T* and *P* range.

DeSain et al. JPCA 2003, Huang et al. PCI 2011

A series of alkenes were studied in this work to capture trends in HO_2 addition to double bonds.

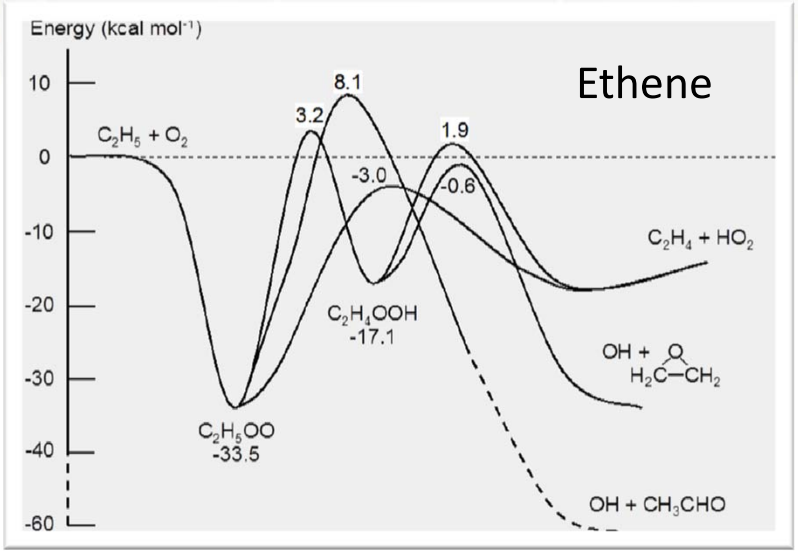


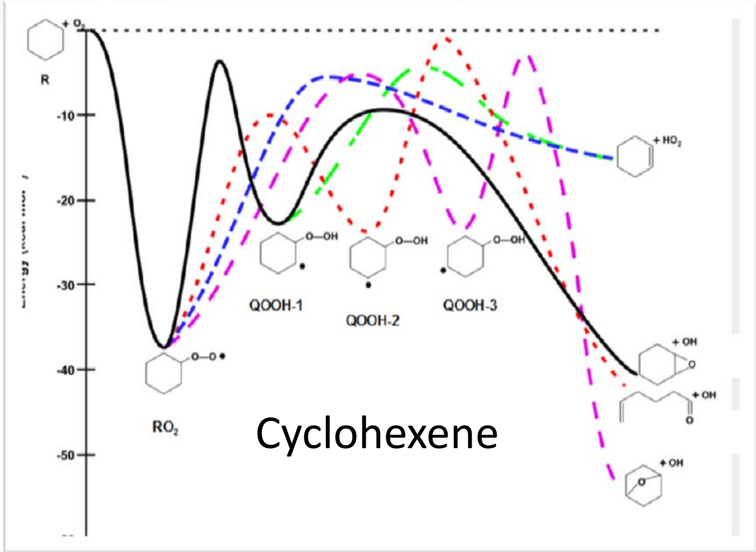
- different C-atom connectivity
- cyclic structure
- allylic H-atom
- heteroatom

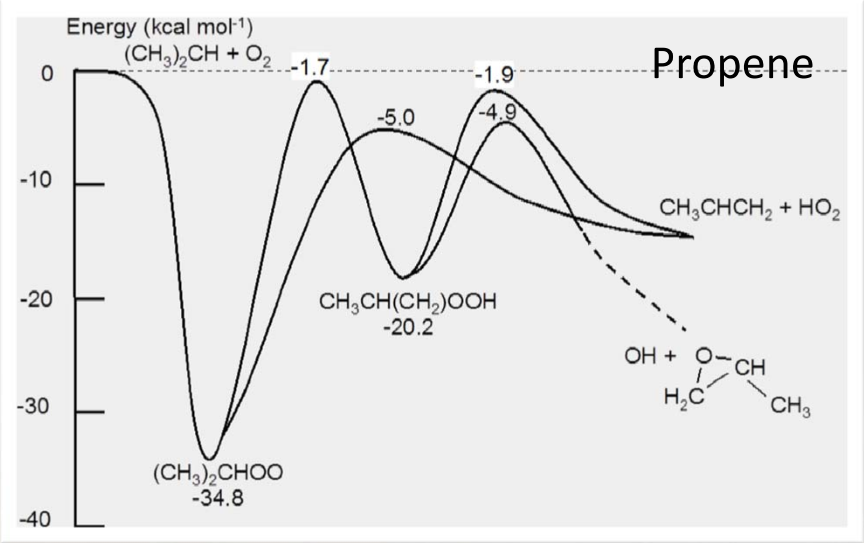
The previously established PES's and methodology was used.

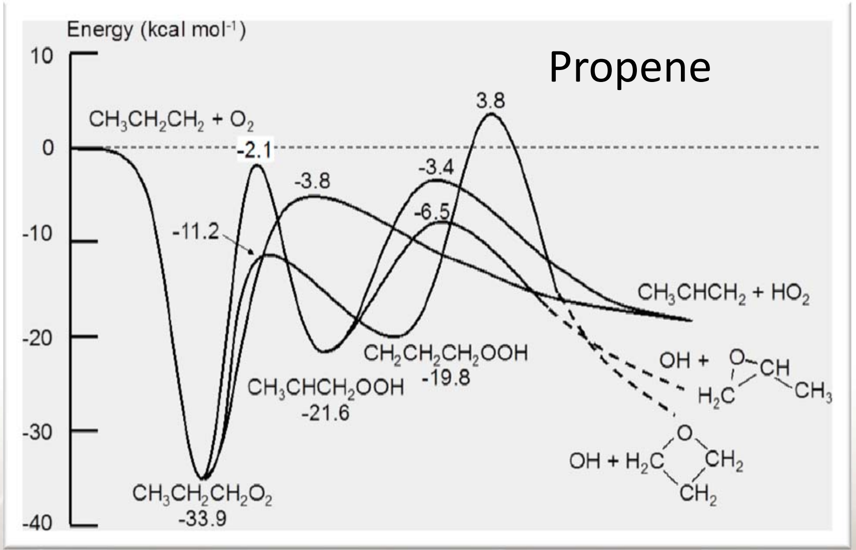
- ~QCISD(T)//B3LYP, including adjustments
- Eckart barriers
- Pitzer-Gwinn type hindering potentials
- same *E*-transfer parameters as in the "forward" direction
- barrier heights for the allylic H-abstraction were determined at the QCISD(T)/cc-PV∞Z//B3LYP/6-311++G(d,p) level of theory

The theoretical framework was based on previously validated PES's.

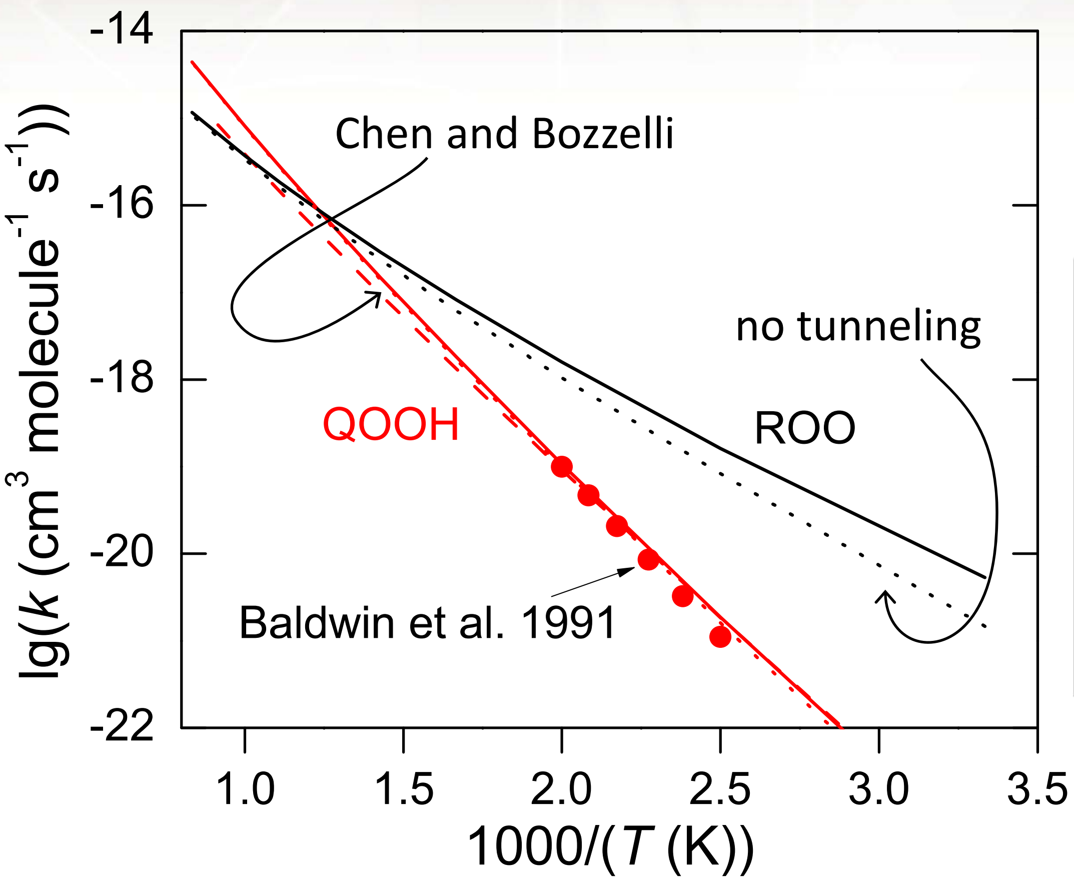

Ethene

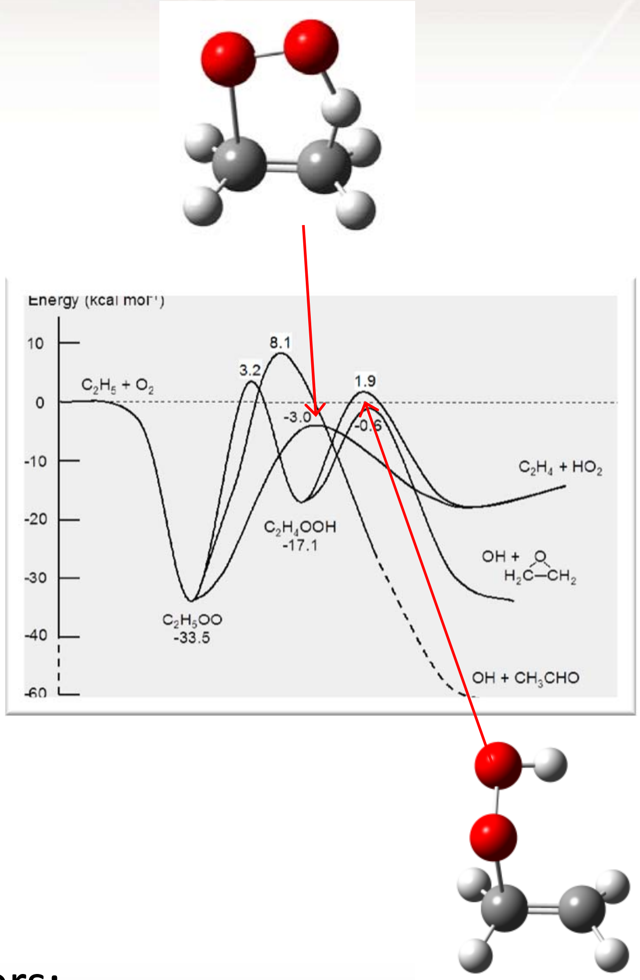

Cyclohexene


Propene


Propene

Ethene + HO$_2$, high-pressure limit

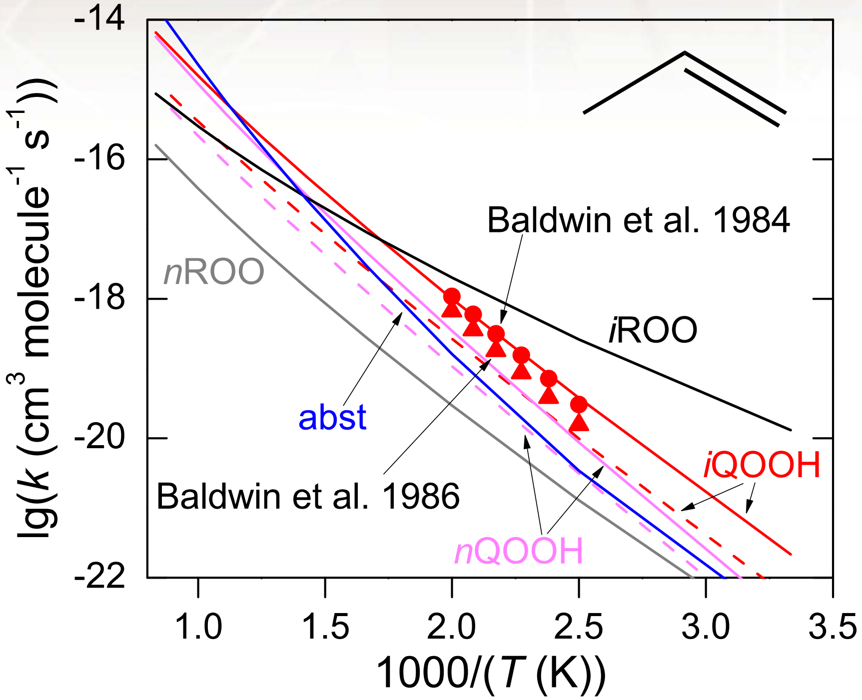


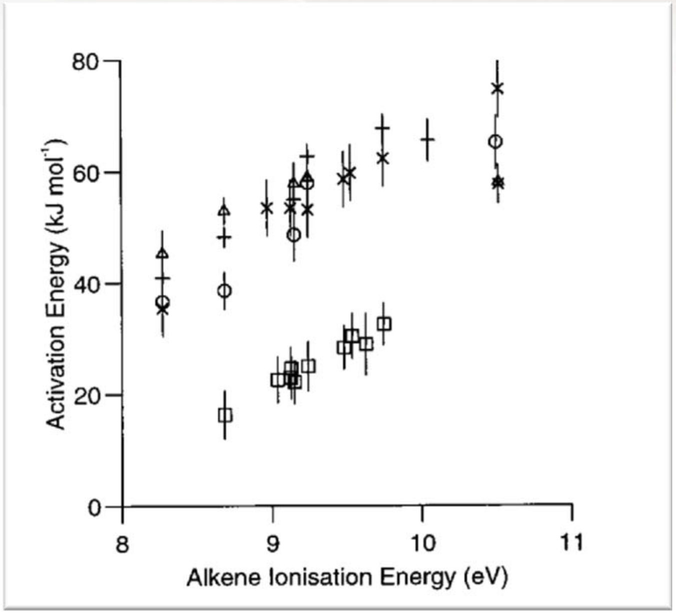


Experiments of Baldwin, Walker and their coworkers: mixtures of alkane, alkene and excess O_2, GC probe.

➔ blind to all channels except the one producing oxirane + OH.

Propene + HO_2, high-pressure limit





Stark, JACS, 122, 2000

Previous studies show a strong correlation between *IE* and *E*≠

➔ the reaction is an electrophilic addition with partial charge transfer at the TS

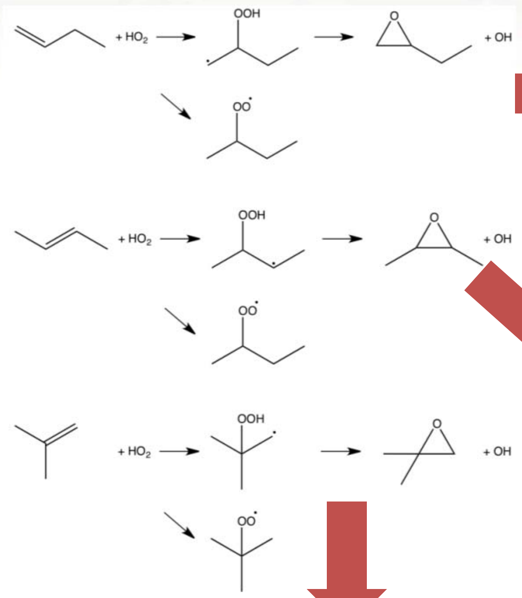
➔ site specificity also has to be correlated with charge transfer

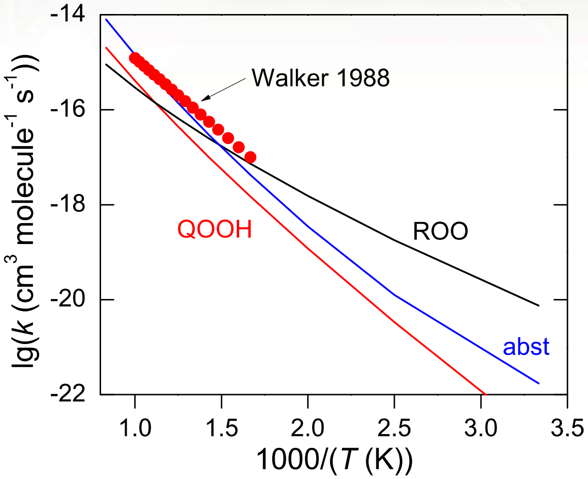
➔ using ESP to calculate point charges:

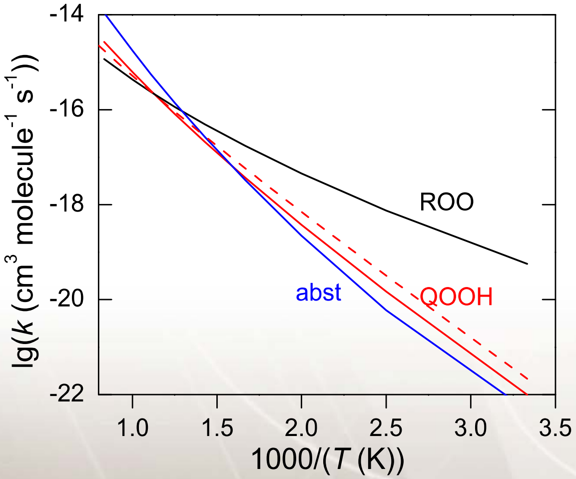
terminal: -0.082
central: -0.141

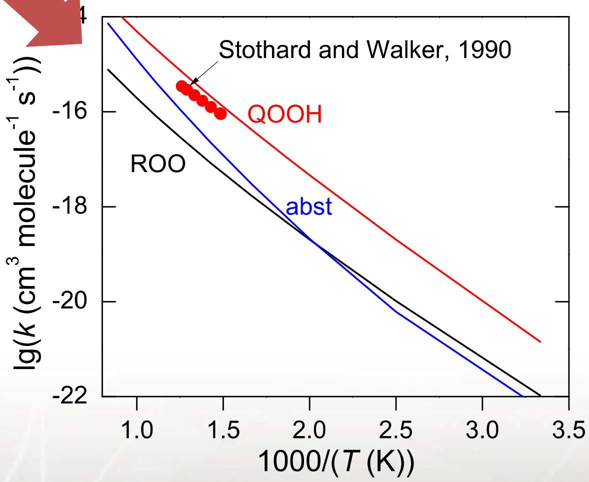
➔ quasi-Markovnikov's rule

Based on the quasi-Markovnikov's rule, simplified PES's were used for the butenes.



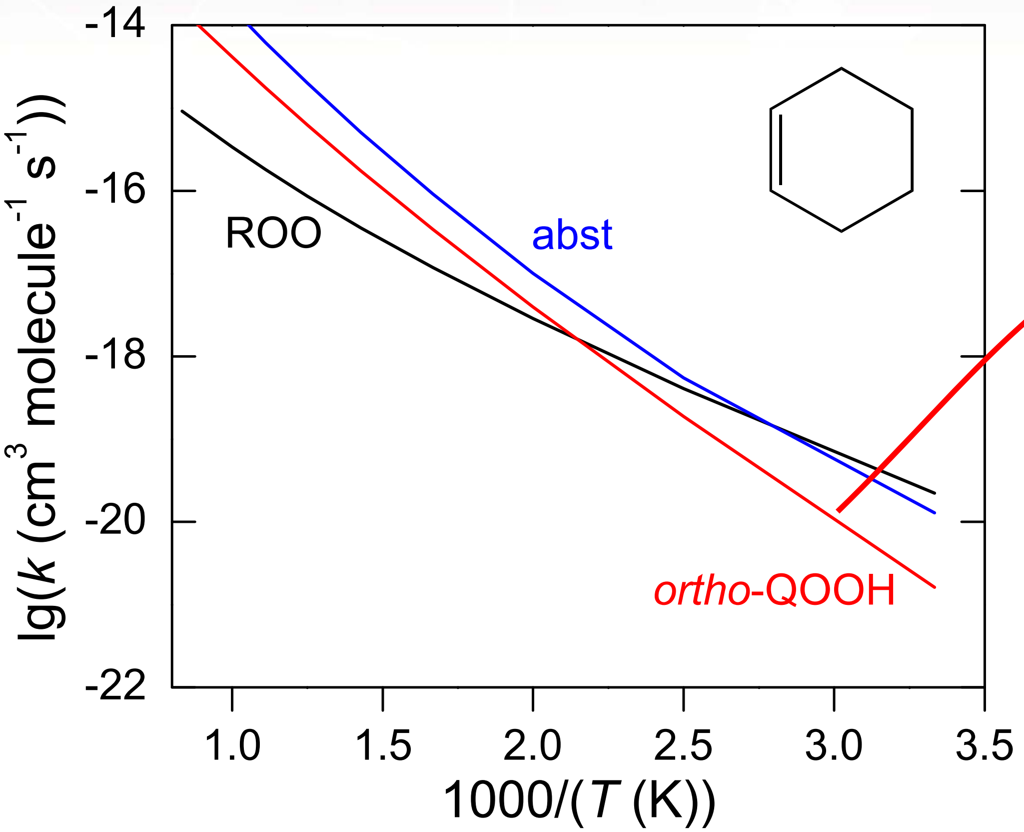




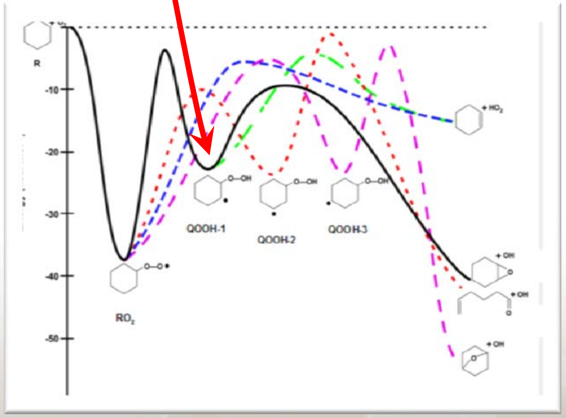


"anomalous"

The alkene + HO_2 reaction alters the importance of the various QOOH's.

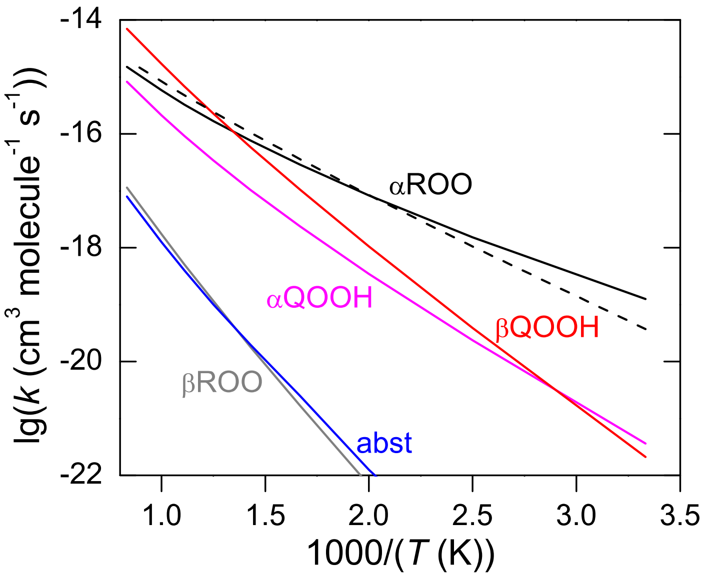


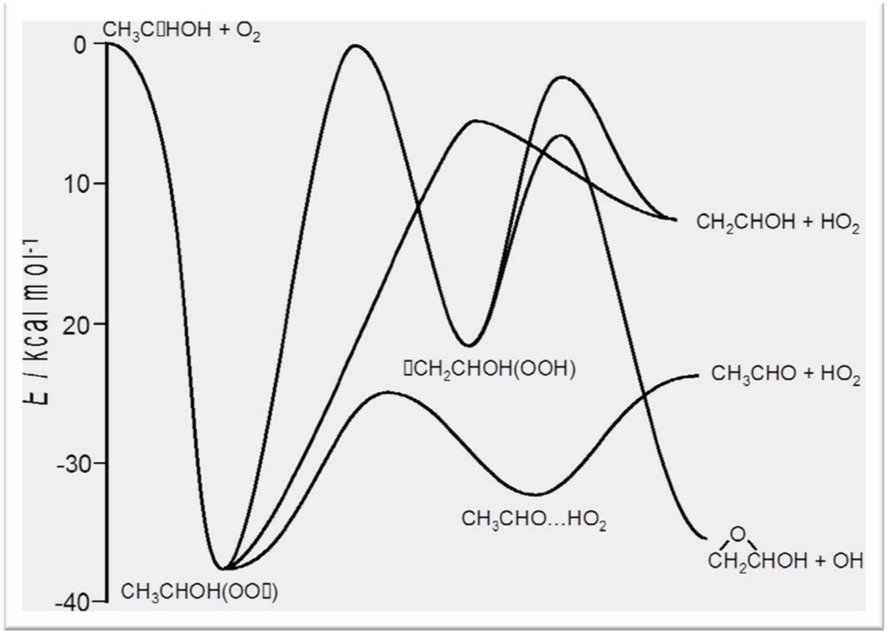
The QOOH accessed from the cyclohexene + HO_2 direction is the one with the smallest branching fraction in the cyclohexyl + O_2 reaction.



HO_2 assisted isomerization of vinyl alcohol to acetaldehyde.

Was first pointed out by Bozzelli and coworkers.



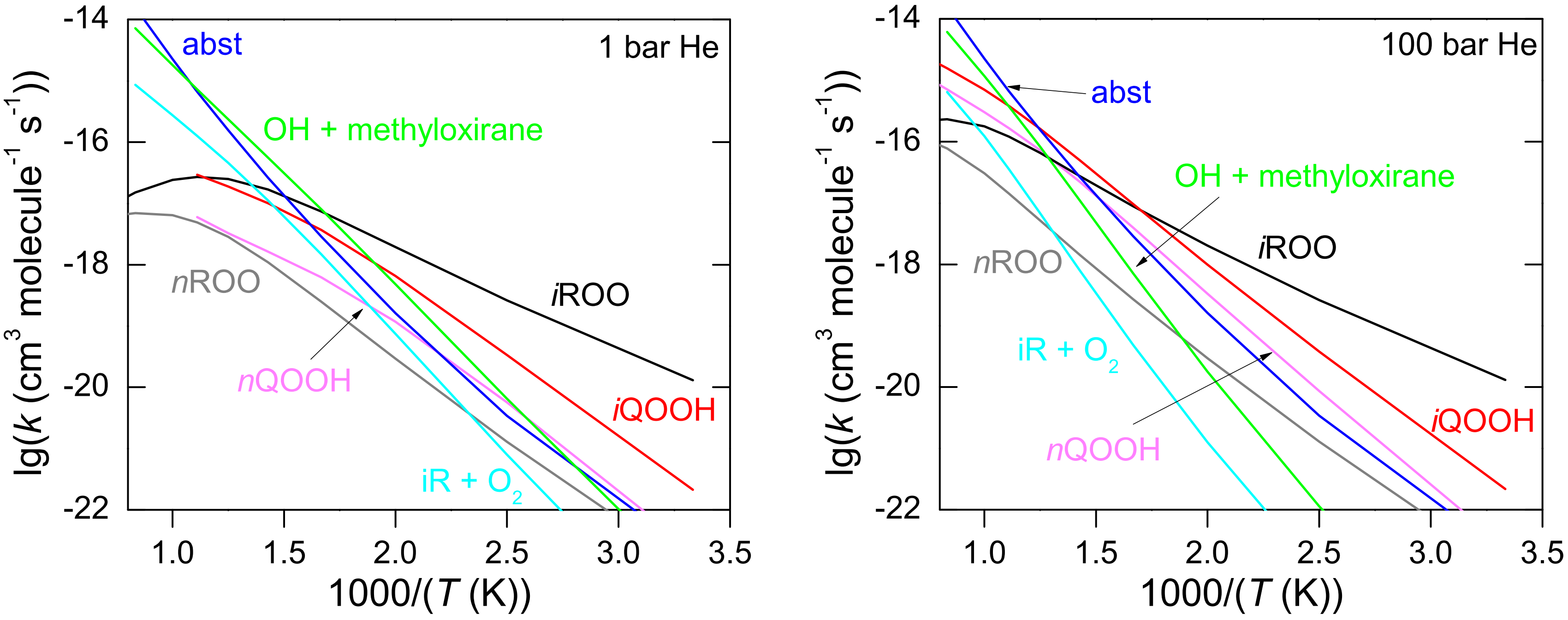


The rate coefficient has to be tested in comprehensive models.

Above ~700 K the QOOH formation is faster than the HO_2 assisted isomerization.

Pressure dependence of alkene + HO_2 reactions.

propene + HO_2

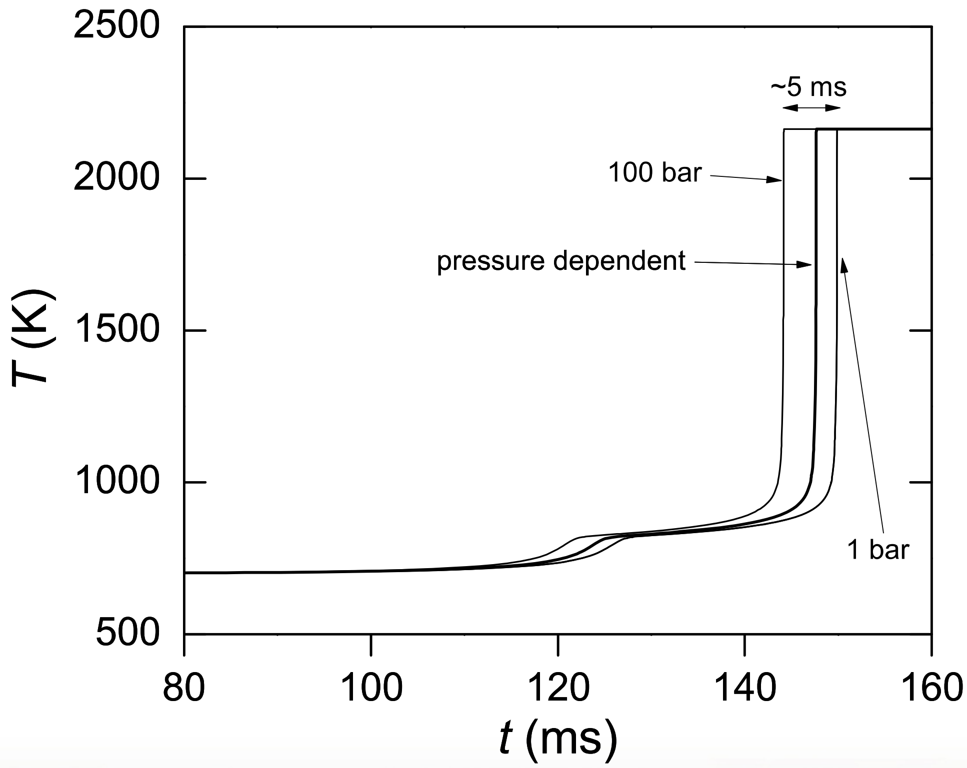


At low *P*/high *T* the lifetime of QOOH is shorter than the characteristic time of collisional relaxation.

At high *P* the QOOH is stabilized and can react with a second O_2 molecule.

The LLNL cyclohexane mechanism was used to study the effect of alkene + HO_2 reaction.

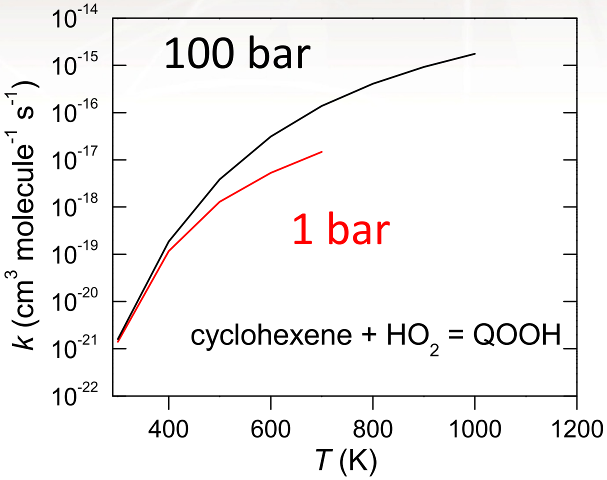
- Mechanism contains 1081 species and 4298 reactions.
- Ignition delay time is calculated, with T_0 = 700 K and P_0 = 10 bar.
- 4:1 mixture of cyclohexane:cyclohexene.

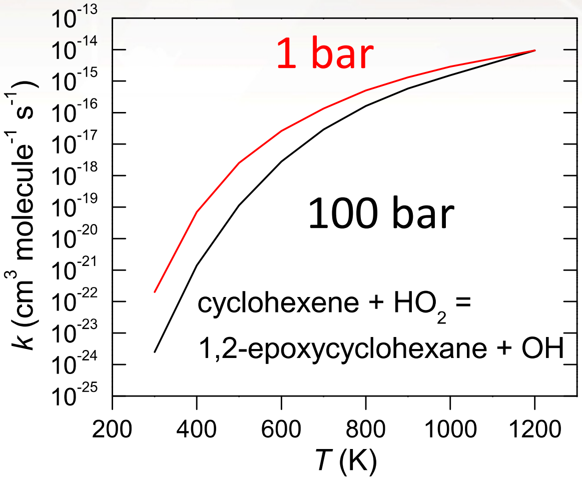


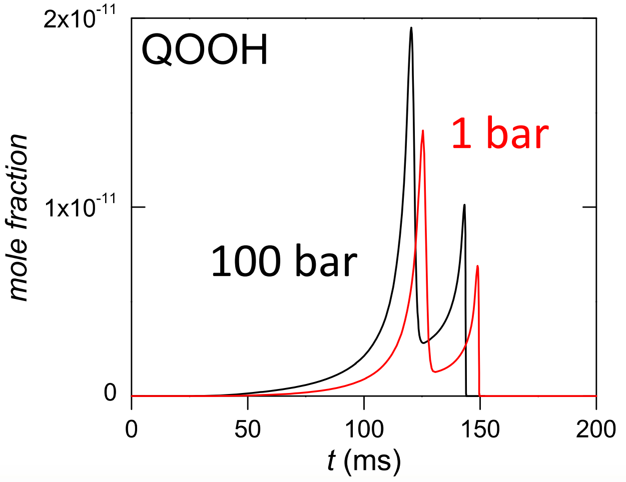
5 ms at 1200 rpm for example is equivalent to 36 degrees in crank angle, which is a significant fraction (1/10) of a stroke!

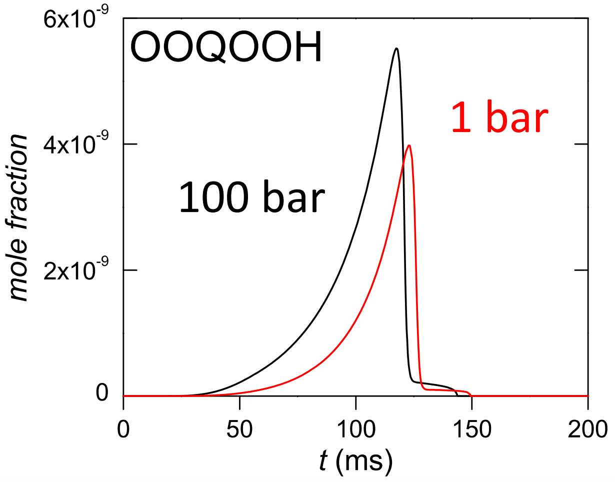
Silke et al. JPCA 2007

At higher pressures QOOH radicals are stabilized to a larger extent.





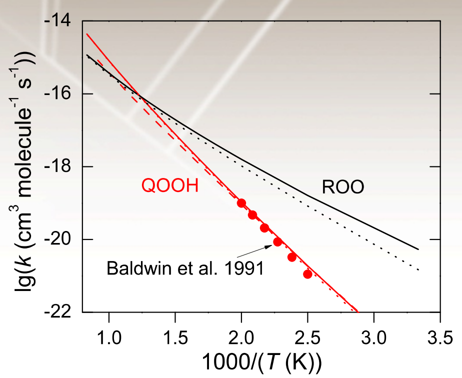




Competition between dissociation and further reaction with O_2 affects the ignition delay times immensely.

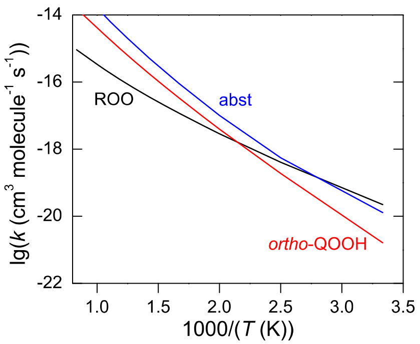
Summary

1. Our calculations are in very close agreement with the measured oxirane + OH channel specific rate coefficients. But it is generally not true that the alkene + HO_2 reaction leads mostly to oxirane and OH!



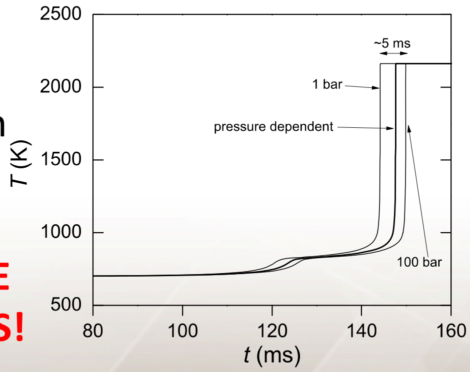
2. In accordance with Chen and Bozzelli we also found that the HO_2 adds almost exclusively to the sp^2 carbon atom with more alkyl groups attached in non-conjugated alkenes.

3. Allylic abstraction is non-negligible from alkenes by HO_2 and competes with the addition reactions.



4. The example of vinyl alcohol + HO_2 shows that substituted alkenes produce a completely different chemistry.

5. We found non-negligible effects arising from the cyclohexene + HO_2 reaction under conditions similar to that of an HCCI engine and with a fuel mixture in which the double to single C-C bond ratio is 1:30.



PRESSURE DEPENDENCE HAS TO BE REPRESENTED IN COMPREHENSIVE CHEMICAL KINETIC MODELS IN ORDER TO GIVE RELIABLE PREDICTIONS!