European Combustion Meeting 2015, Budapest

What do we Really Know about the Low-Temperature Oxidation of Alkanes ?

F. Battin-Leclerc

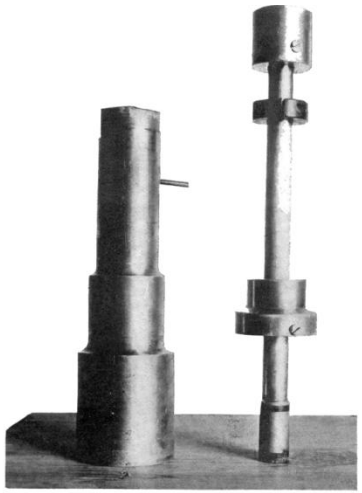
Why study Low-Temperature Oxidation (LTO) chemistry?

- A fascinating subject of scientific interest for many years certainly because it describes intriguing experimental features

Autoignition

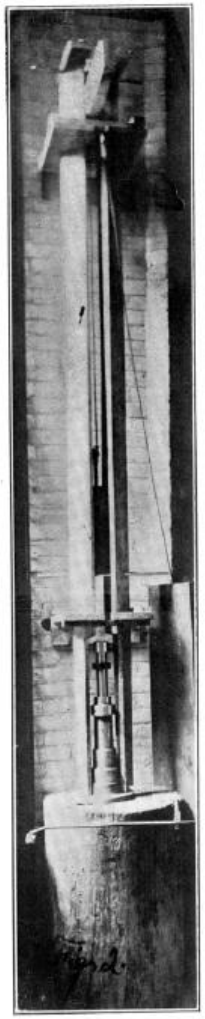
First rapid compression machines built in 1906 (G. Falk, JACS, 1906-1907)

G. Vanhove, RCM, Workshop, 2012



"In order to heat the gas whose ignition temperature was to be determined, it was necessary to enclose it in a small vessel supplied with a device for allowing the gas to be compressed instantaneously"

To cause adiabatic compression, a weight of 25 kg was dropped on the piston from heights of48 to 86 cm.



Why study LTO chemistry?

- A fascinating subject of scientific interest for more than 100 years which describes intriguing experimental features

Cool flames

First observed in 1817 by Sir Humphry Davy

J. Griffiths, New Scientist, 2004

In a flow reactor

C_2H_6

In a static reactor

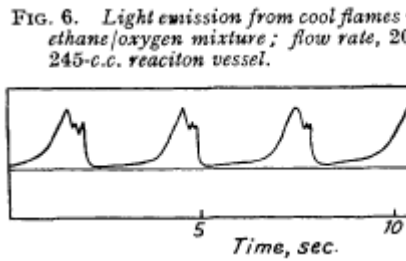


FIG. 6. *Light emission from cool flames in a 75/25 ethane/oxygen mixture; flow rate, 20 c.c./sec.; 245-c.c. reaciton vessel.*

J.A. Gray, J. Chem. Soc., 1953

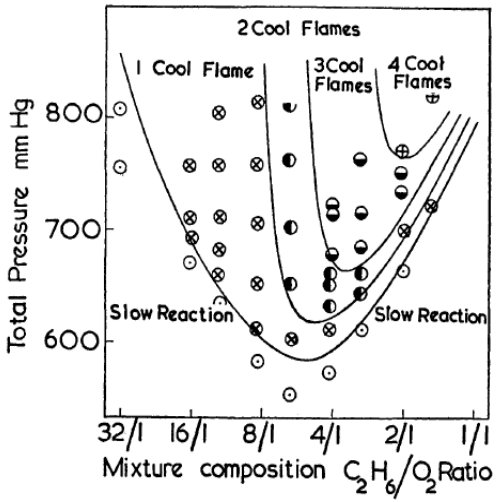


FIG. 4.—Pressure/composition limits for single and multiple cool flames in ethane + oxygen mixtures at 330° C.

J.A. Knox and G.W. Norrish, Trans. Farad. Soc., 1954

Why study LTO chemistry?

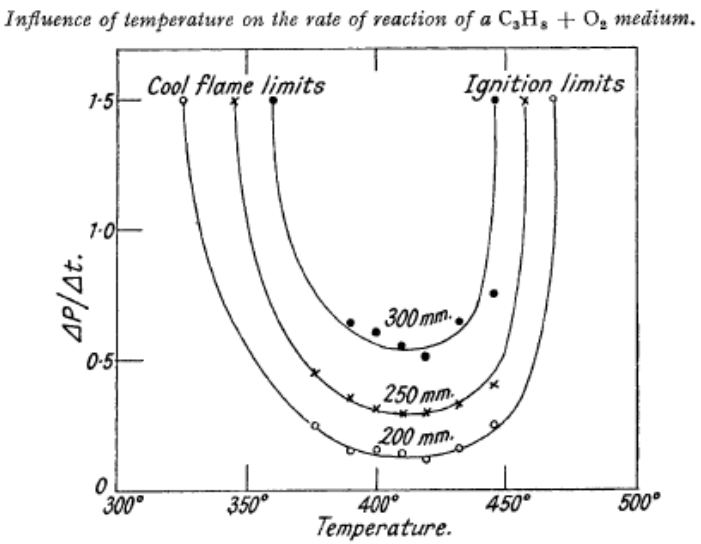
- A fascinating subject of scientific interest for about100 years which describes intriguing experimental features

Negative temperature coefficient (NTC)

First mentioned in 1929 (R.N. Pease, JACS)

Measurements in static reactors

C_3H_8, $\phi = 5$



D.M. Newitt and L.S. Thornes, J. Chem. Soc., 1937

C_2H_6, $\phi = 3.5$

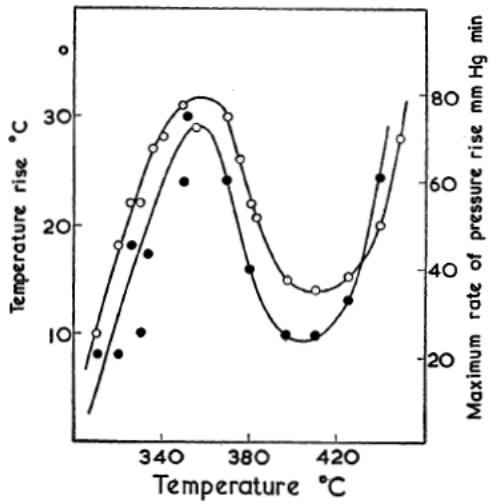
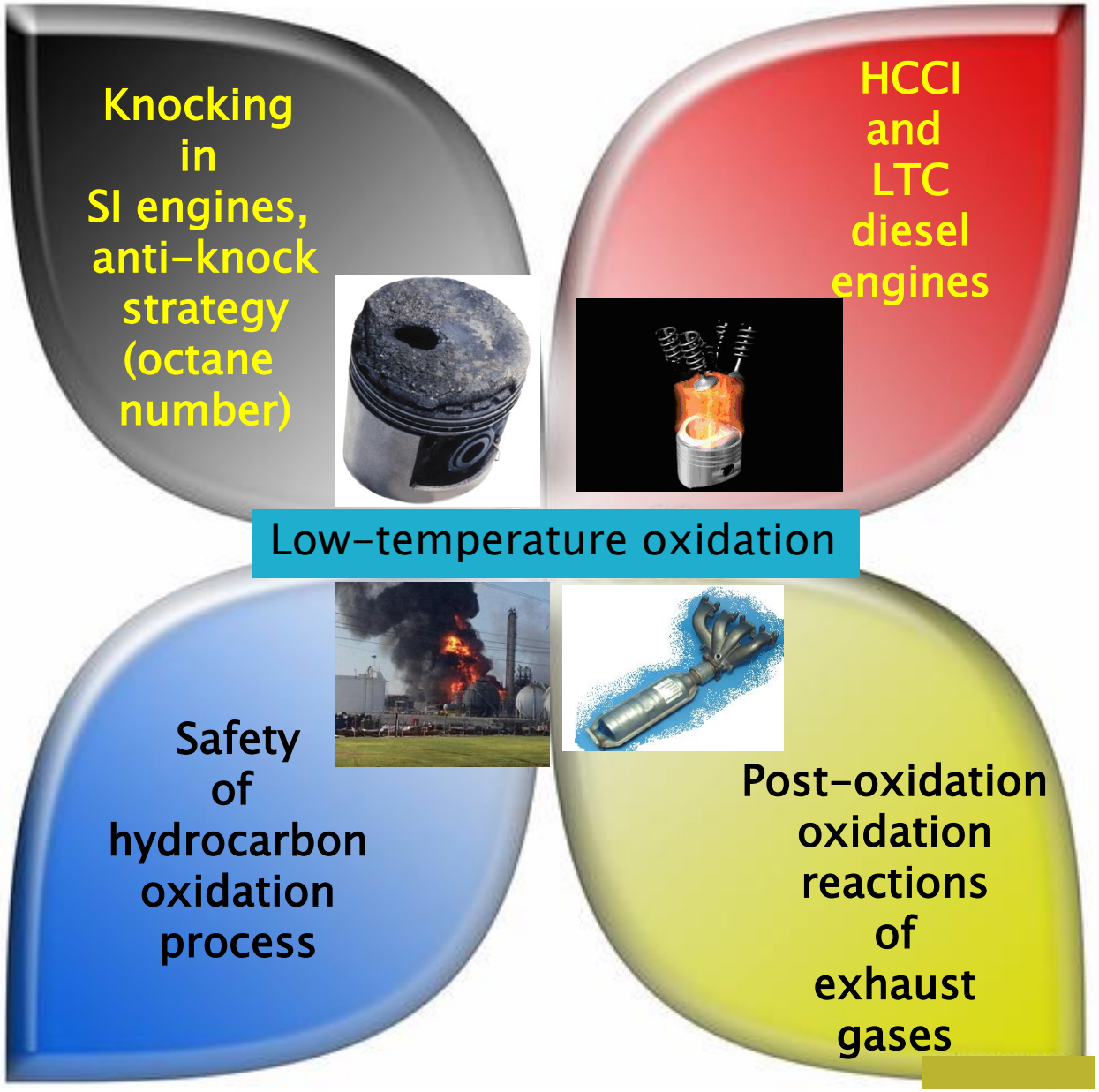


FIG. 1.—Rate of slow oxidation of equimolecular ethane + oxygen mixtures at different temperatures in a 5 cm diam. Pyrex reaction vessel.
⊙ temperature rise; ● maximum rate of pressure rise.

J.A. Knox and G.W. Norrish, Trans. Farad. Soc., 1954

Why study LTO chemistry?

- A subject with important practical applications

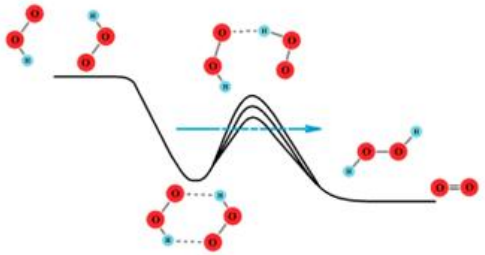


Why study LTO chemistry?

- **A subject with important practical applications:**

How LTO kinetics can influence engine performances

$HO_2 + HO_2 = H_2O_2 + O_2$

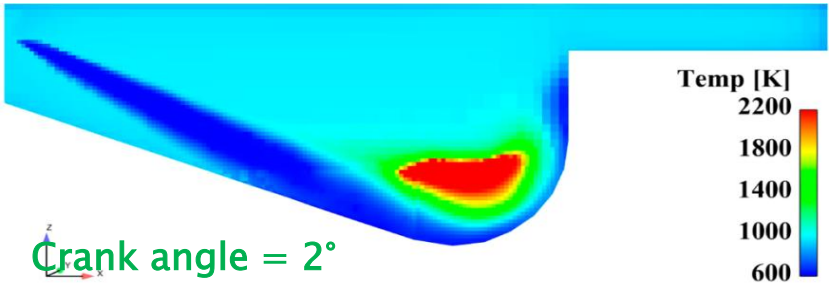


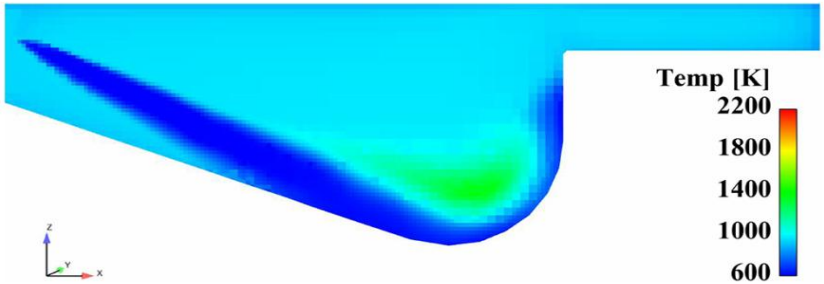
Caterpillar single cylinder engine

S. Som, M.J. Davis et al., J. Phys. Chem. Letters, 2013

CFD predicted spatial temperature distribution
in a diesel engine fed by a
n–heptane/ methyl butanoate mix. (869 reactions)

Tunneling not considered in rate constant calculation





Tunneling considered in rate constant calculation

Many detailed kinetic models of LTO

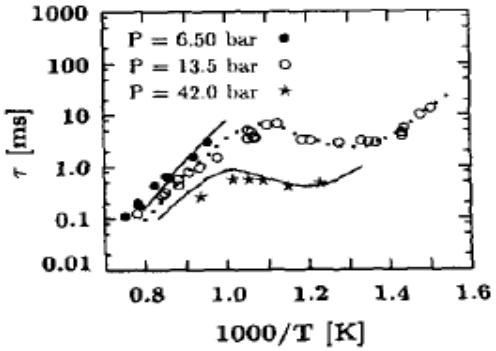
- **Autoignition of fuel representative of gasoline available since the end of the 90s**

Autoignition of *n*-heptane

in a shock tube (Aachen) and a rapid compression machine (Lille)

Symbols correspond to experiments and lines to simulations (ϕ = 1, P from 3 to 42 bar)

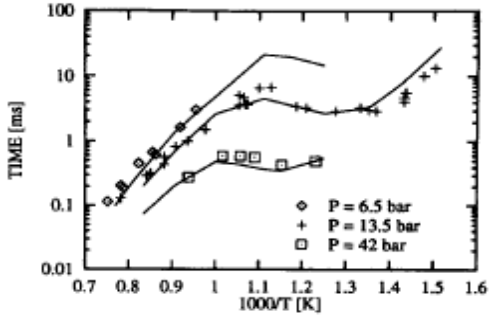
Livermore



H.J. Curran, C.K. Westbrook et al.
Combust. Flame 1998

550 species and 2450 reactions

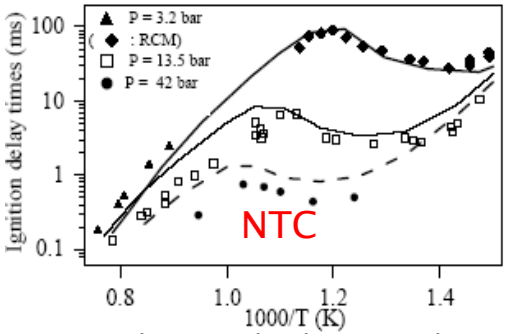
Milano



E. Ranzi, P. Dagaut et al.
Combust. Flame 1995

100 species and 2000 reactions

Nancy



F. Buda, P.A. Glaude, V. Warth,
F. Battin-Leclerc et al.
Combust. Flame 2005

360 species and 1820 reactions

Automatic generation

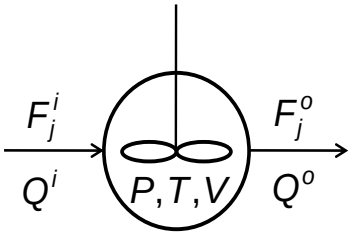
Models lead to similar agreement for reproducing the available experimental results, but with very different LTO kinetics

Many detailed kinetic models of LTO

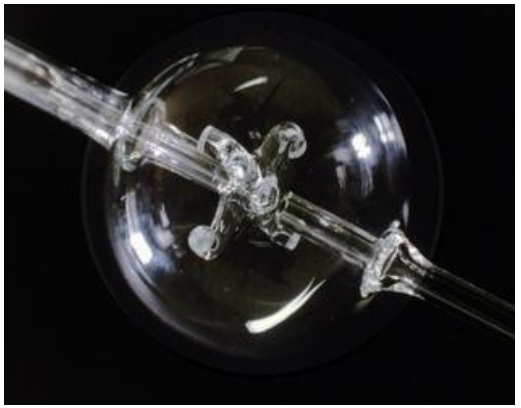
- **Model validation for product formation often using jet-stirred reactor (JSR) data**

O. Herbinet and G. Dayma., chapter 8, in Cleaner Combustion; Battin-Leclerc, F.; Simmie, J. M.; Blurock, E., Eds.; Green Energy and Technology; Springer London, 2013

Orléans

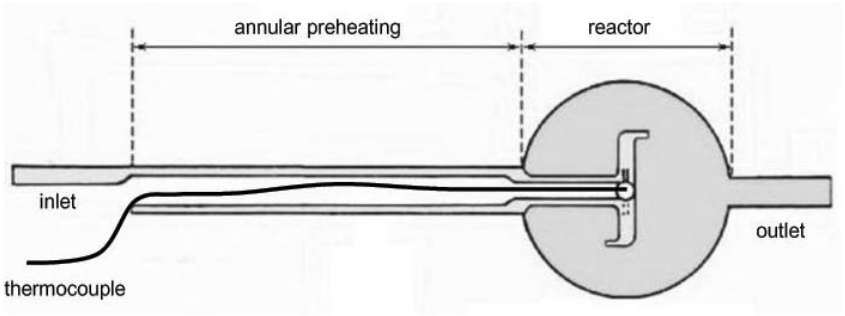


Perfect material mixing
if based on the design
of D. Matras and J. Villermaux
Chem Eng Sci 1973



Nancy

Reactor when locating heating resistance wires in Nancy



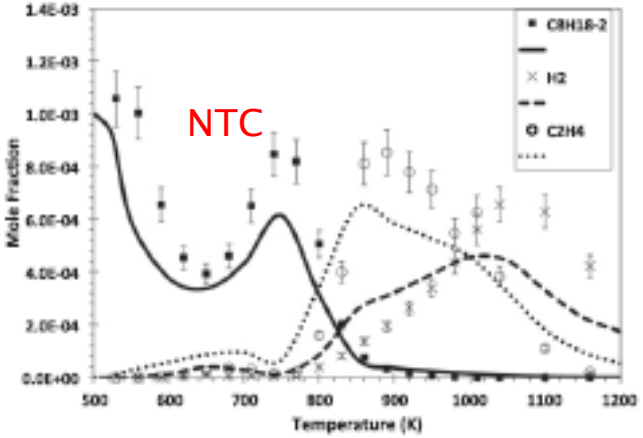
Thermal homogeneity
if preceeding by a preheating zone
and used with high dilution

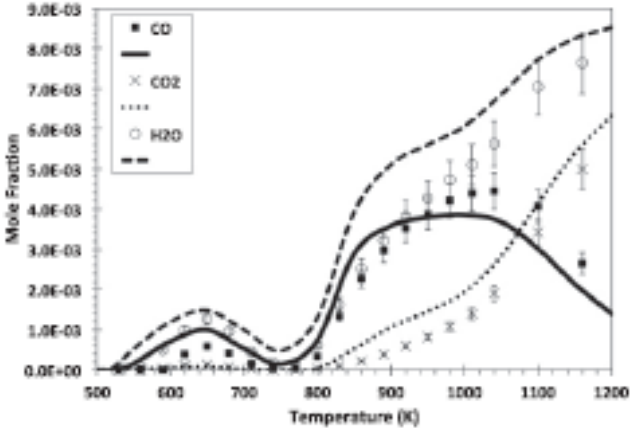
Many detailed kinetic models of LTO

- **Models can predict JSR major product formation**

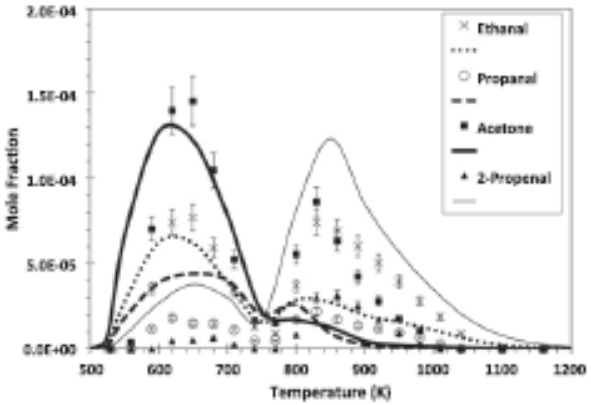
Oxidation of 2-methylheptane

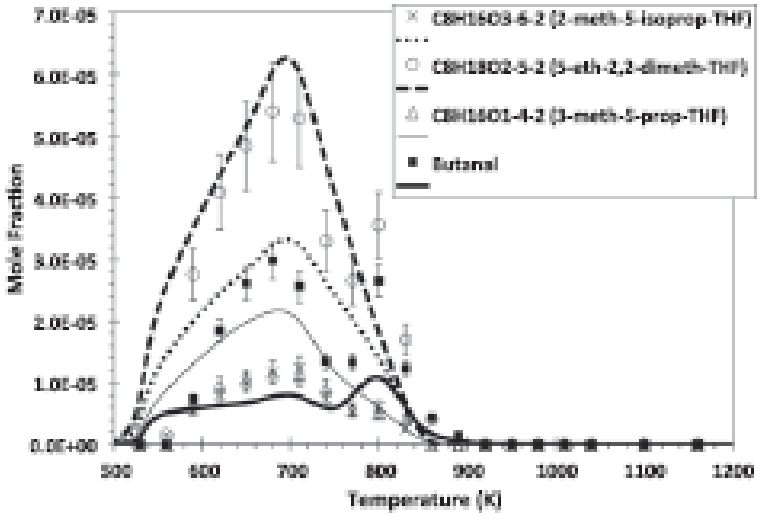
Symbols correspond to experiments and lines to simulations
($\phi = 1$, P = 10 bar, $\tau = 0.7$ s, **0.1 %** initial fuel, GC measurements)





S.M. Sarathy, C.K.Westbrook, P. Dagaut et al. Combust. Flame 2011



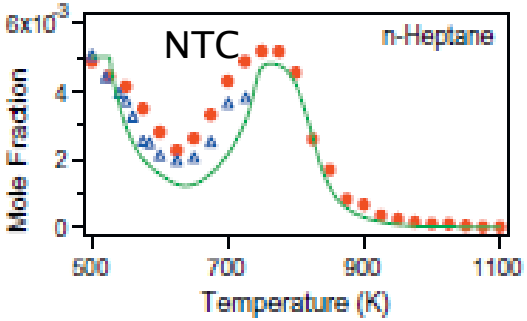


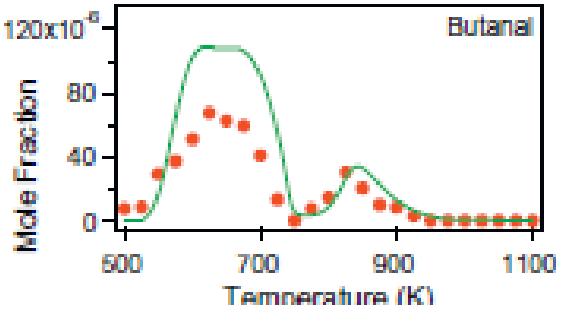
Many detailed kinetic models of LTO

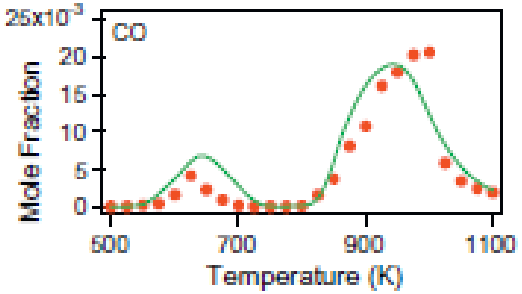
- **Models can predict JSR major product formation**

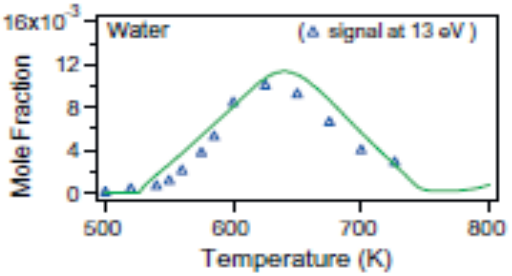
Oxidation of *n*-heptane

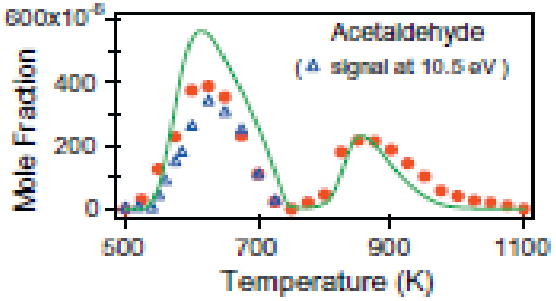
Symbols correspond to experiments and lines to simulations
($\phi = 1$, P = 1 bar, $\tau = 2$ s, **0.5 %** initial fuel,
GC (red) and PI-MS (blue) measurements)

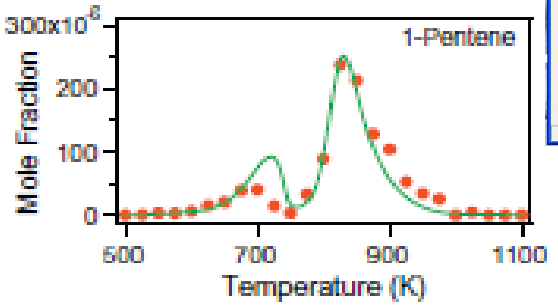


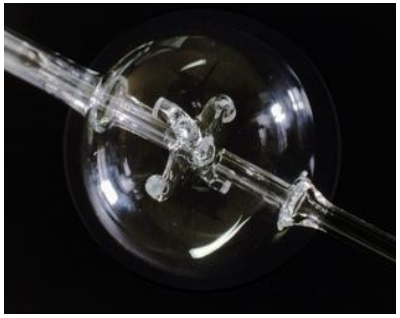




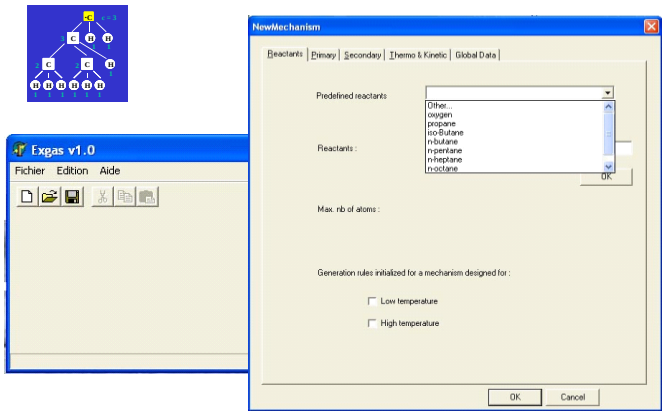








O. Herbinet, Z. Serinyel, V. Warth, F. Battin-Leclerc, F. Qi et al. Combust. Flame 2012

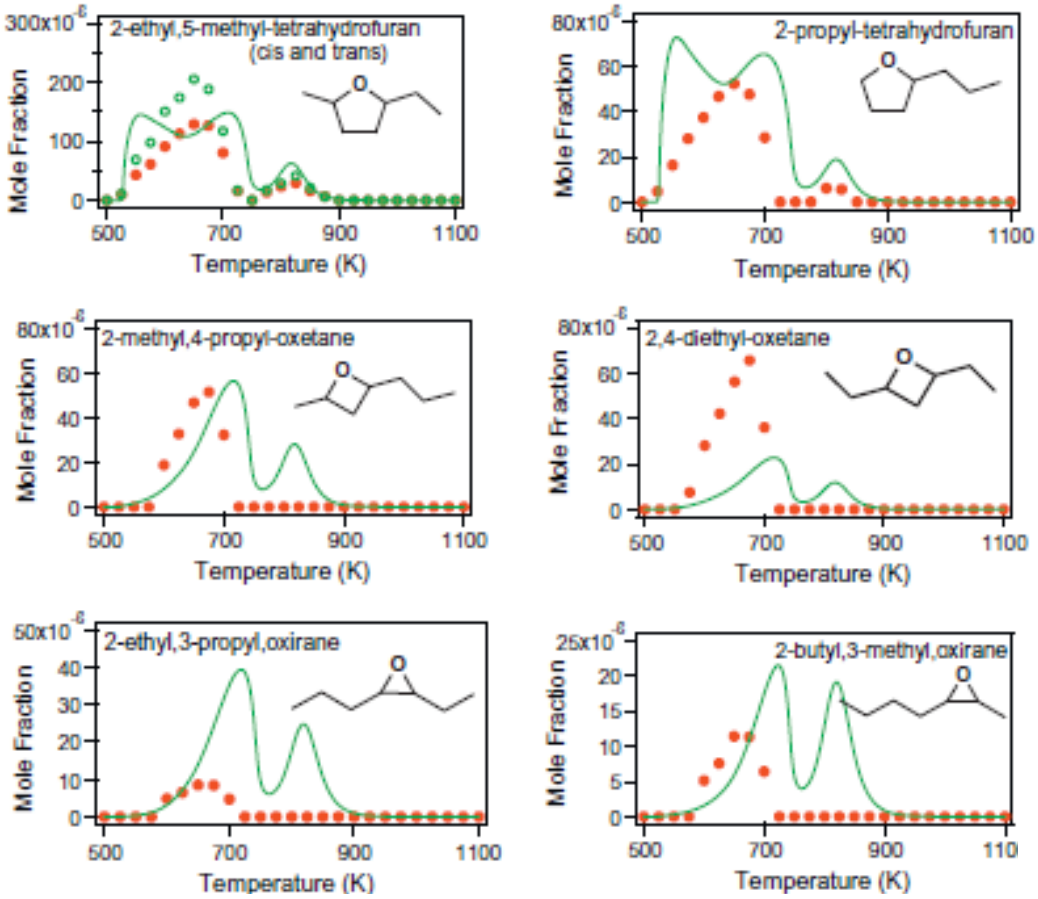


Many detailed kinetic models of LTO

- **Models cannot predict all JSR minor product formation**

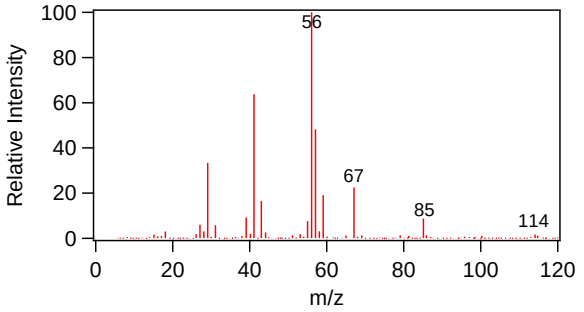
Oxidation of *n*-heptane

Symbols correspond to experiments and lines to simulations
($\phi = 1$, P = 1 bar, $\tau = 2$ s, **0.5 %** initial fuel, GC measurements)

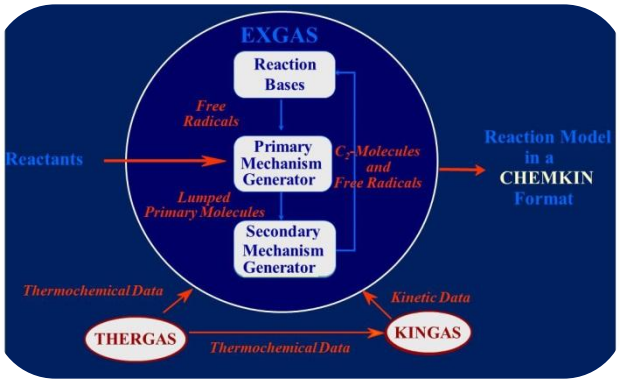


O. Herbinet, Z. Serinyel, V. Warth, F. Battin-Leclerc, F. Qi et al. Combust. Flame 2012

Electron impact mass spectrum of 2,4-diethyl-oxetane



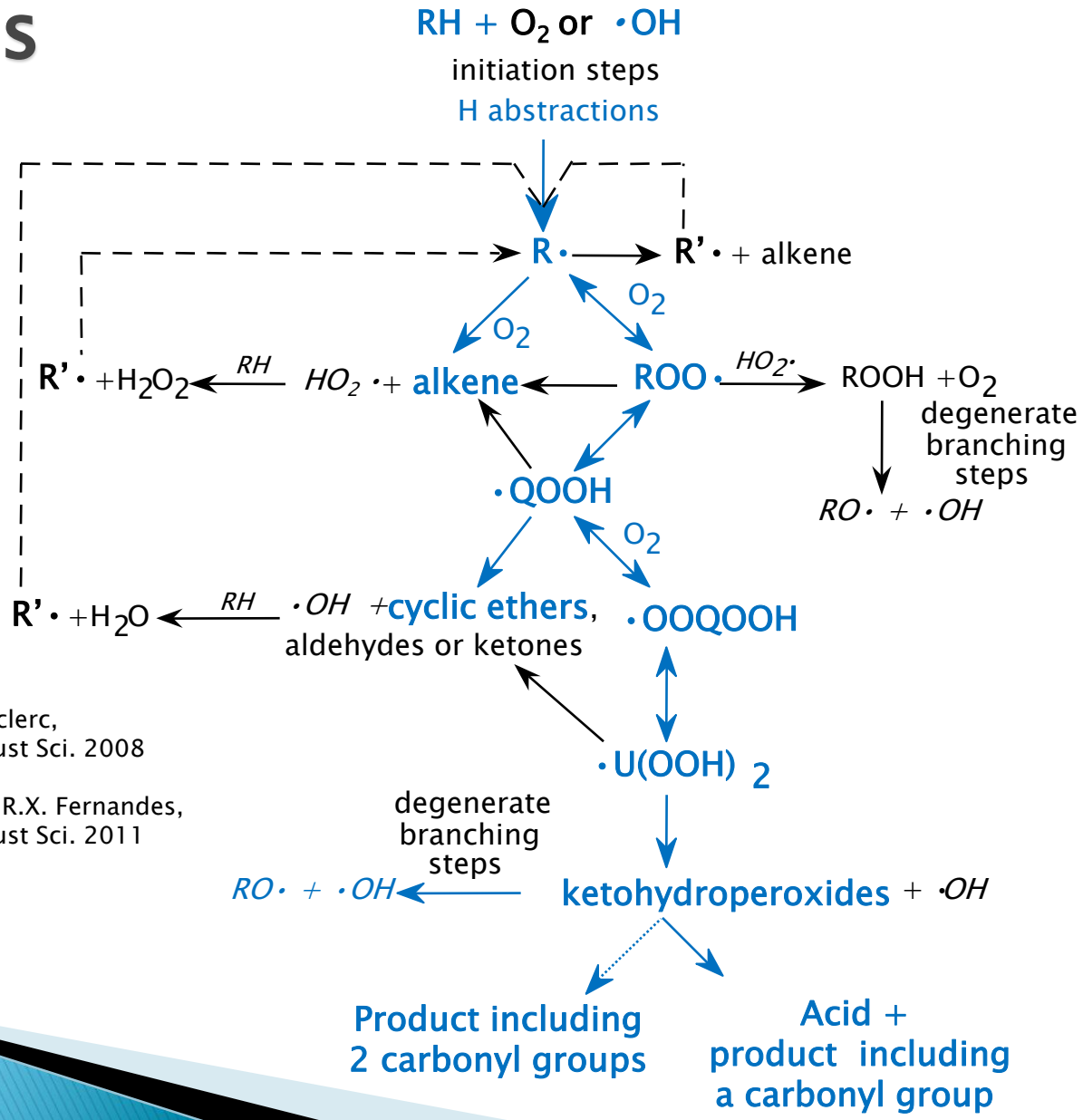
O. Herbinet, F. Battin-Leclerc et al., Fuel, 2011



More deviations in non-stoichiometric mixtures

Always need of kinetic parameter adjustments

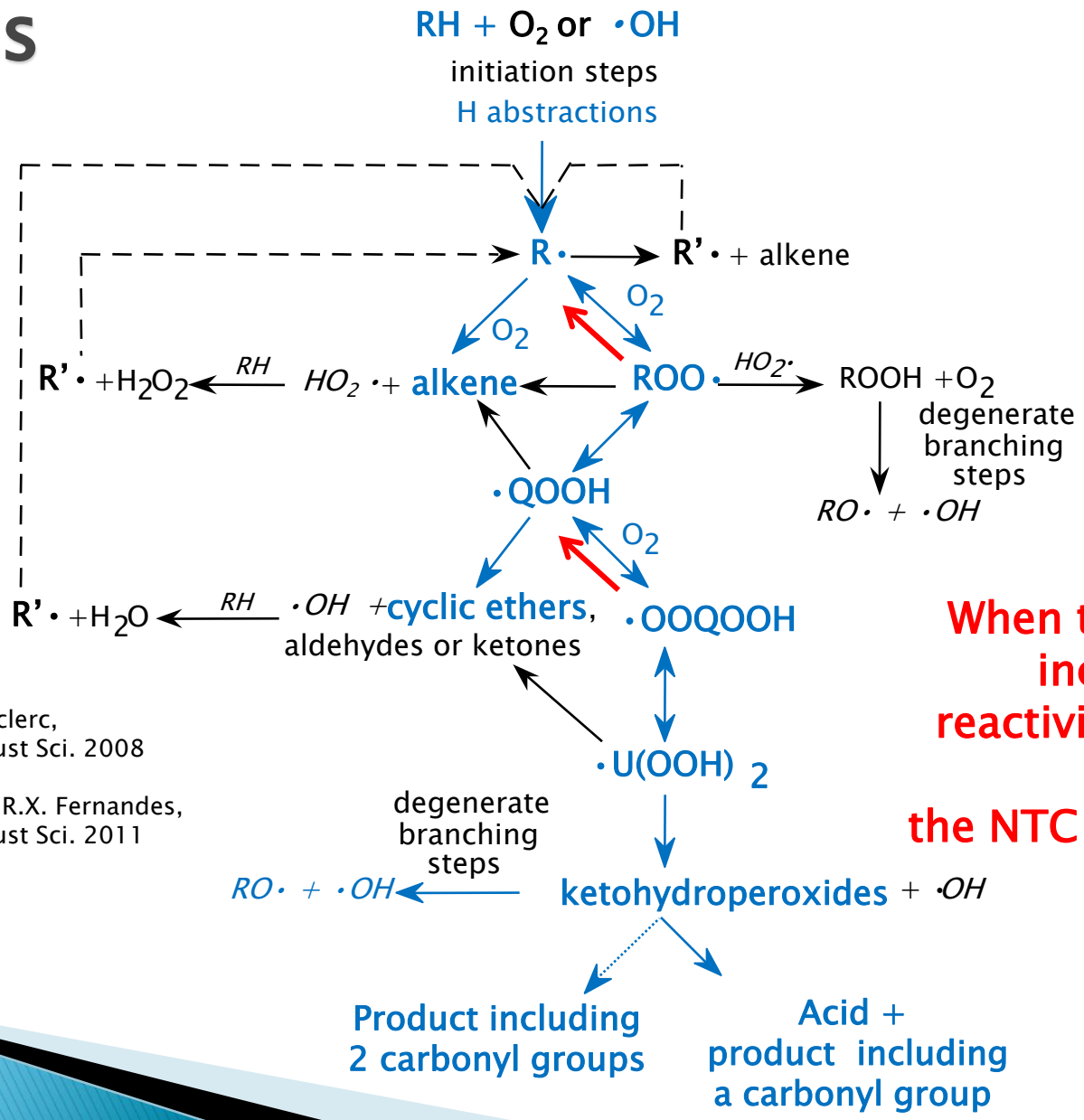
Chemical knowledge used in alkane LTO models



F. Battin-Leclerc,
Prog. Energ. Combust Sci. 2008

J. Zádor, C.A. Taatjes, R.X. Fernandes,
Prog. Energ. Combust Sci. 2011

Chemical knowledge used in alkane LTO models

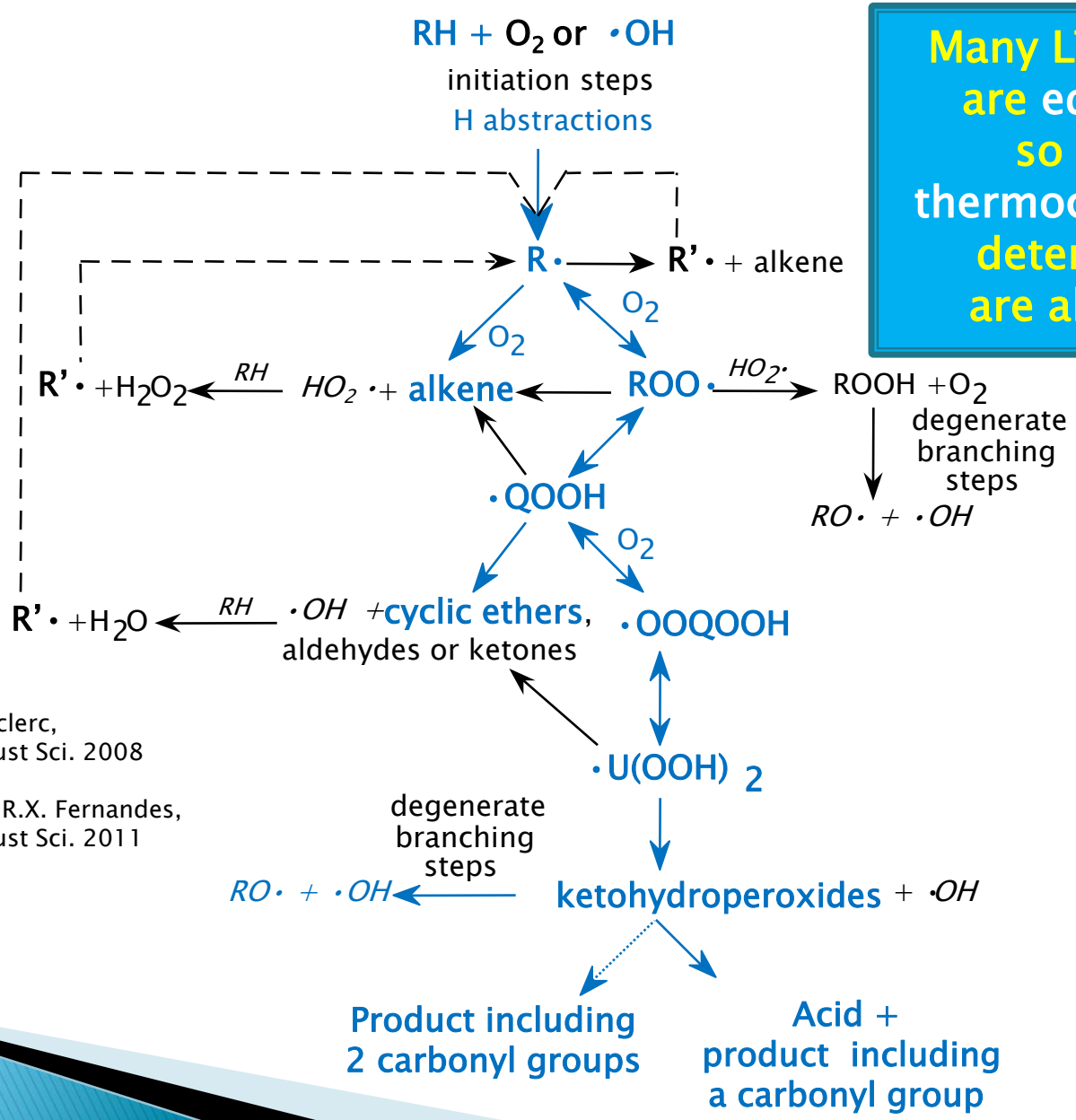


F. Battin-Leclerc,
Prog. Energ. Combust Sci. 2008

J. Zádor, C.A. Taatjes, R.X. Fernandes,
Prog. Energ. Combust Sci. 2011

When temperature increases, reactivity decreases and the NTC zone appears

Origin of kinetics used in alkane LTO models



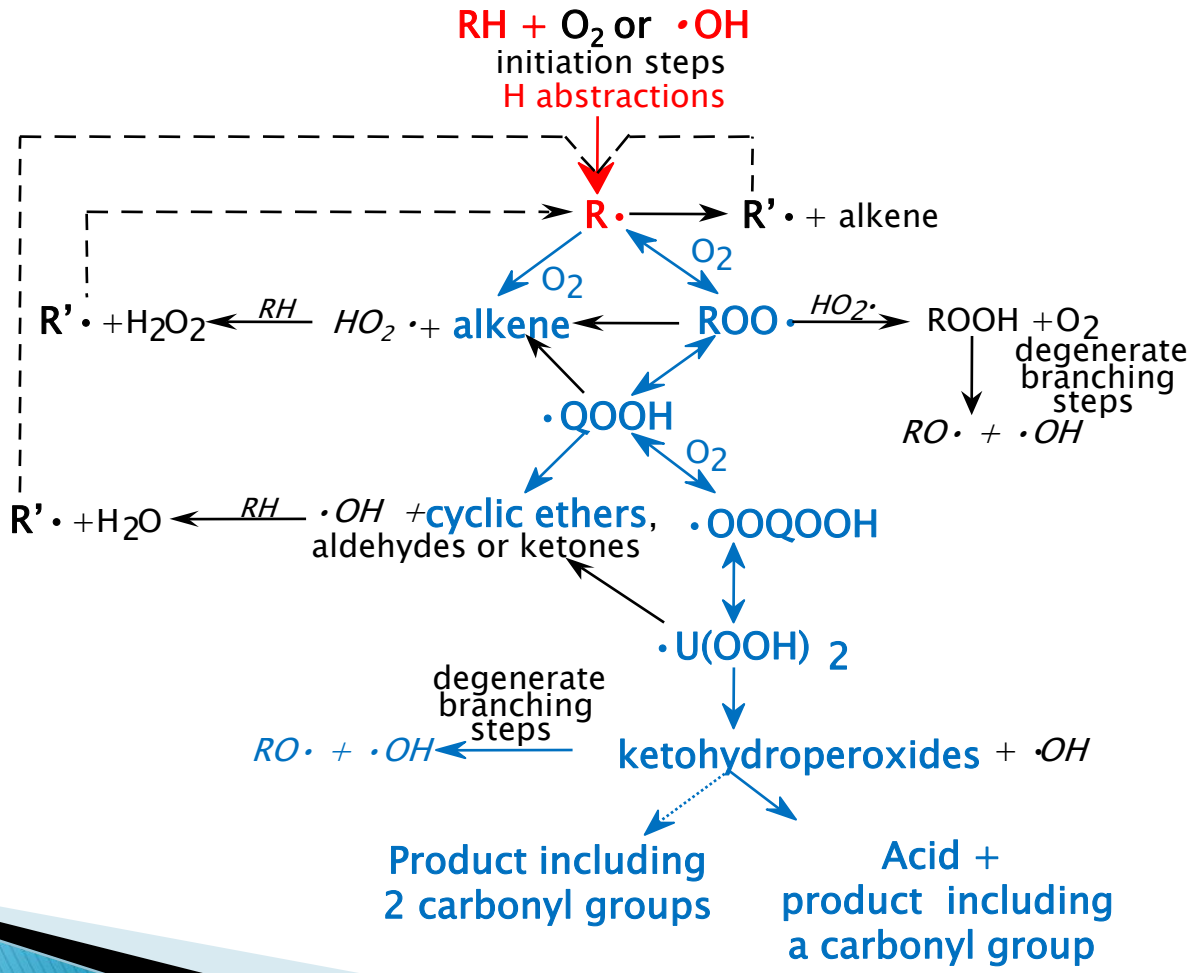
F. Battin-Leclerc,
Prog. Energ. Combust Sci. 2008

J. Zádor, C.A. Taatjes, R.X. Fernandes,
Prog. Energ. Combust Sci. 2011

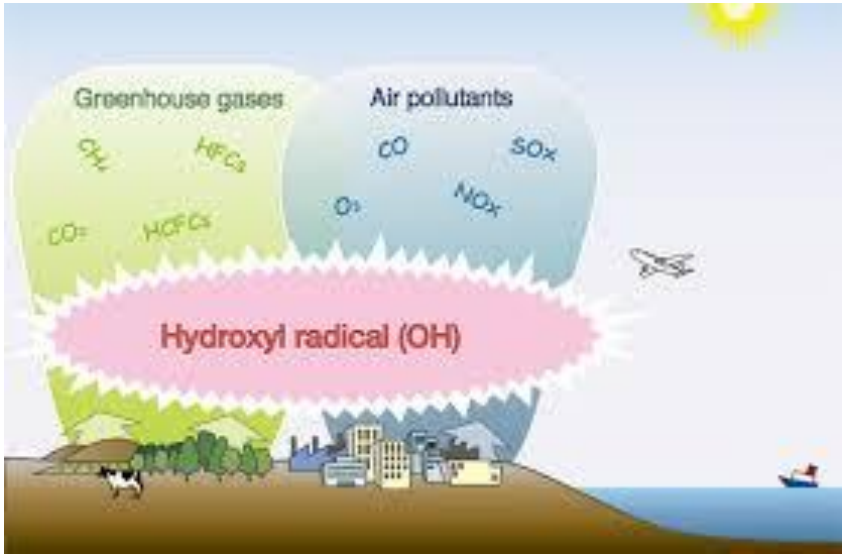
Many LTO reactions are equilibrated, so accurate thermochemical data determinations are also needed

Origin of kinetics used in alkane LTO models

- **Hydrogen atom abstractions from fuel**



Hydrogen atom abstractions from fuel: OH radicals

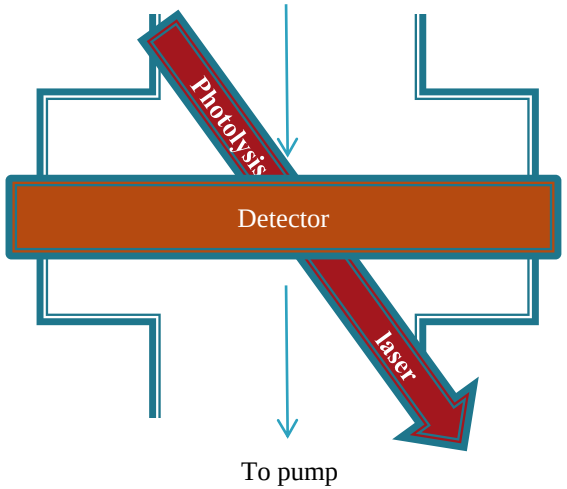


OH radicals have
a determinant role
in atmospheric chemistry

Many measurements
of the rate constant
of OH + X = XH + H_2O
(3159 records in NIST kinetics data base)

Laser flash photolysis

Reactant
+ radical precursor (O_3, HNO_3, H_2O_2…)
+ carrier gas

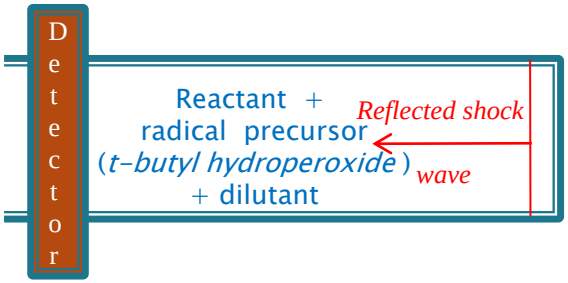


Often by
Laser
Induced
Fluorescence

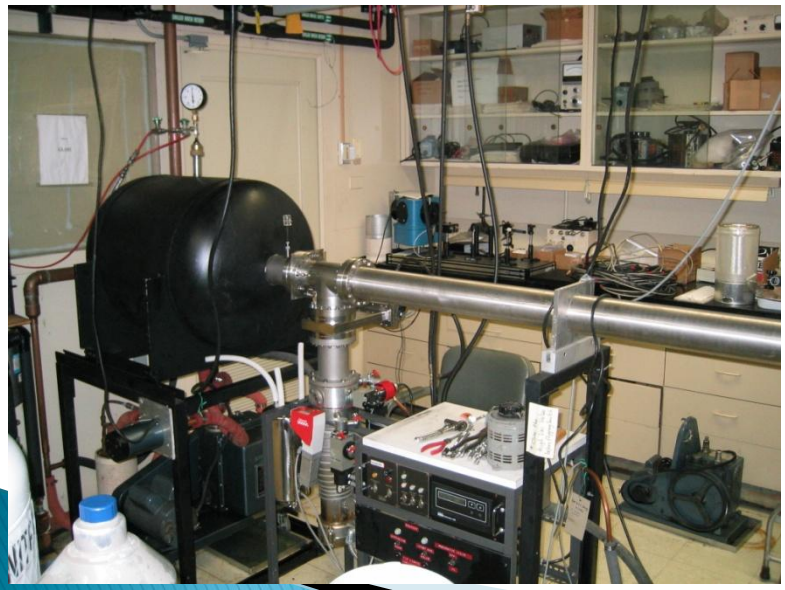
but mostly below 400 K
and for C_1–C_3 alkanes

Hydrogen atom abstractions from fuel: OH radicals

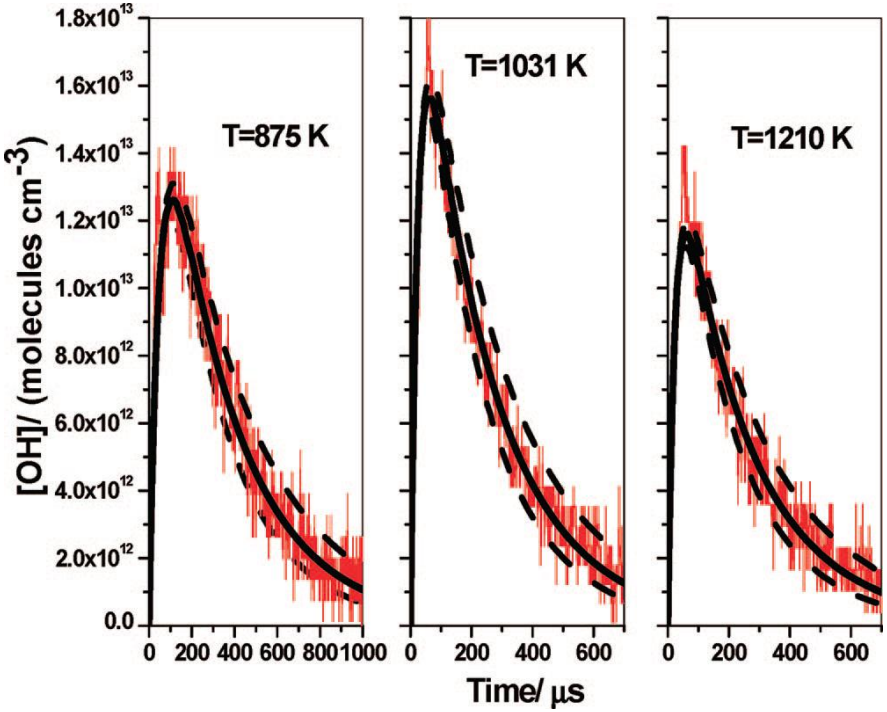
- C_2–C_7 alkane high temperature study using a shock tube



By courtesy of R.S.tranter and J.V. Michael



R. Sivaramakrishnan and J.V. Michael, JPCA 2009



OH absorption profiles for $k_{OH + n\text{-heptane}}$

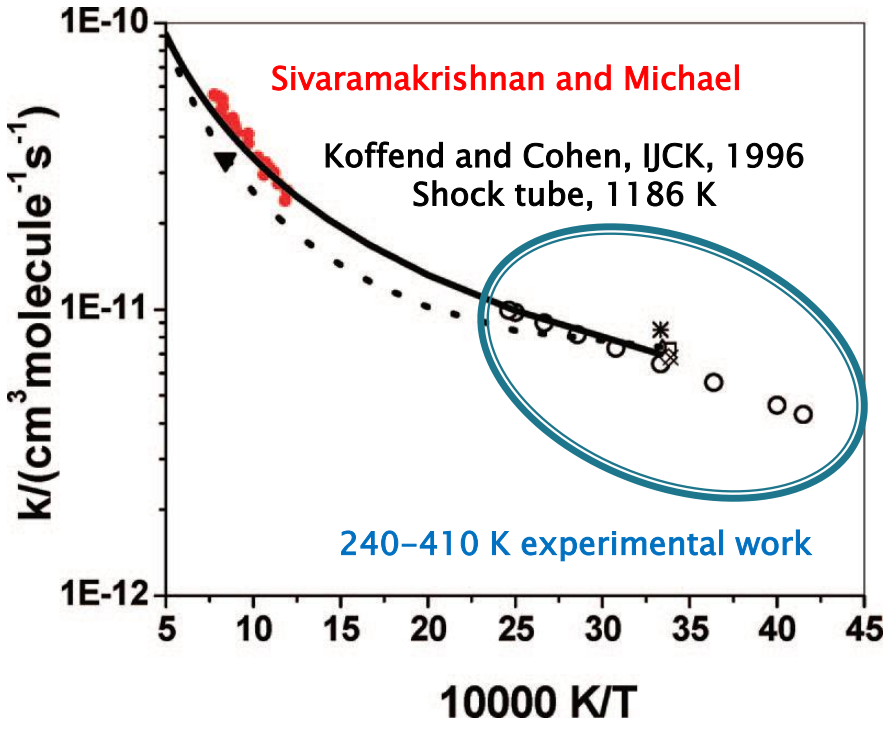
Experimental measurements and rate constant fitting from a 49 step mechanism.

The dashed lines are fits with changes in $k_{OH + n\text{-heptane}}$ by $\pm$20%.

Hydrogen atom abstractions from fuel: OH radicals

- **High temperature study using a shock tube for 9 linear and branched C_2–C_7 alkanes**

R. Sivaramakrishnan and J.V. Michael, JPCA 2009



Arrhenius plot of $k_{OH + n\text{-heptane}}$

$k_{OH + Alkanes}$ (298–2000 K)
Experimentally studied,
obtained from derived group additivity correlations

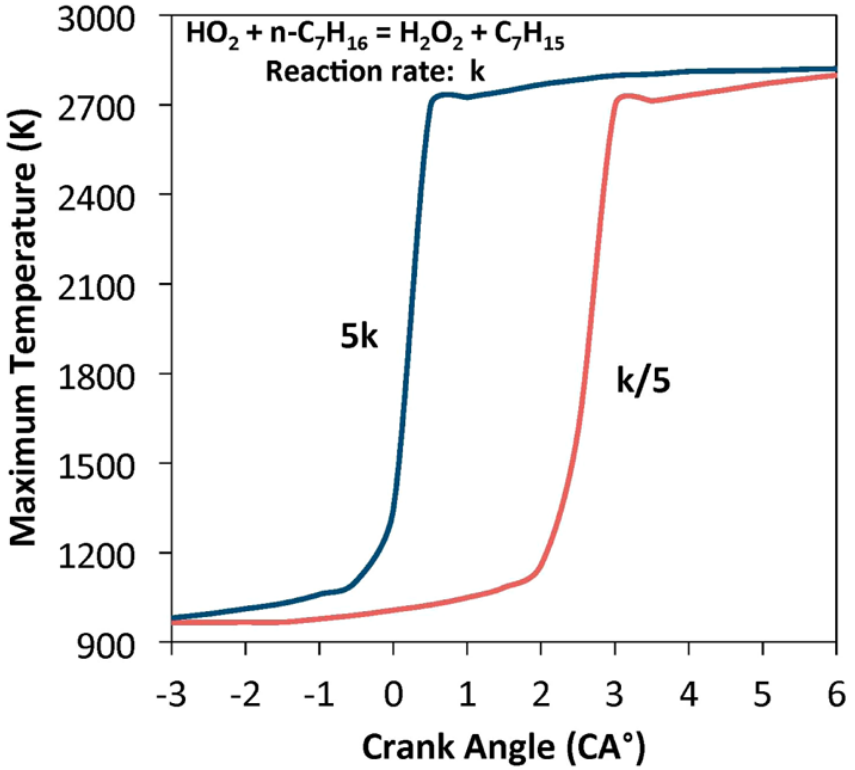
molecule	A	n	B
ethane	2.680×10^{-18}	2.224	373
propane	2.419×10^{-17}	1.935	91
n-butane	8.499×10^{-16}	1.475	139
i-butane	6.309×10^{-19}	2.414	−381
n-pentane	2.495×10^{-16}	1.649	−80
neo-pentane	1.090×10^{-16}	1.763	374
n-hexane	1.398×10^{-16}	1.739	−202
2,3-dimethylbutane	2.287×10^{-17}	1.958	−365
n-heptane	9.906×10^{-16}	1.497	−96
n-octane	4.186×10^{-15}	1.322	−19
neo-octane	1.636×10^{-16}	1.763	374
n-nonane	1.290×10^{-14}	1.186	40
n-decane	3.012×10^{-14}	1.087	84
n-undecane	5.284×10^{-14}	1.025	111
n-dodecane	9.325×10^{-14}	0.960	139
n-tridecane	1.508×10^{-13}	0.907	163
n-tetradecane	2.278×10^{-13}	0.862	183
n-pentadecane	3.262×10^{-13}	0.823	201
n-hexadecane	4.474×10^{-13}	0.789	216

More studies on large alkanes are needed

Hydrogen atom abstractions from fuel: other radicals

- RO_2 and HO_2 radicals are also present in large amounts at low-temperatures

Influence on CFD predictions in a diesel engine

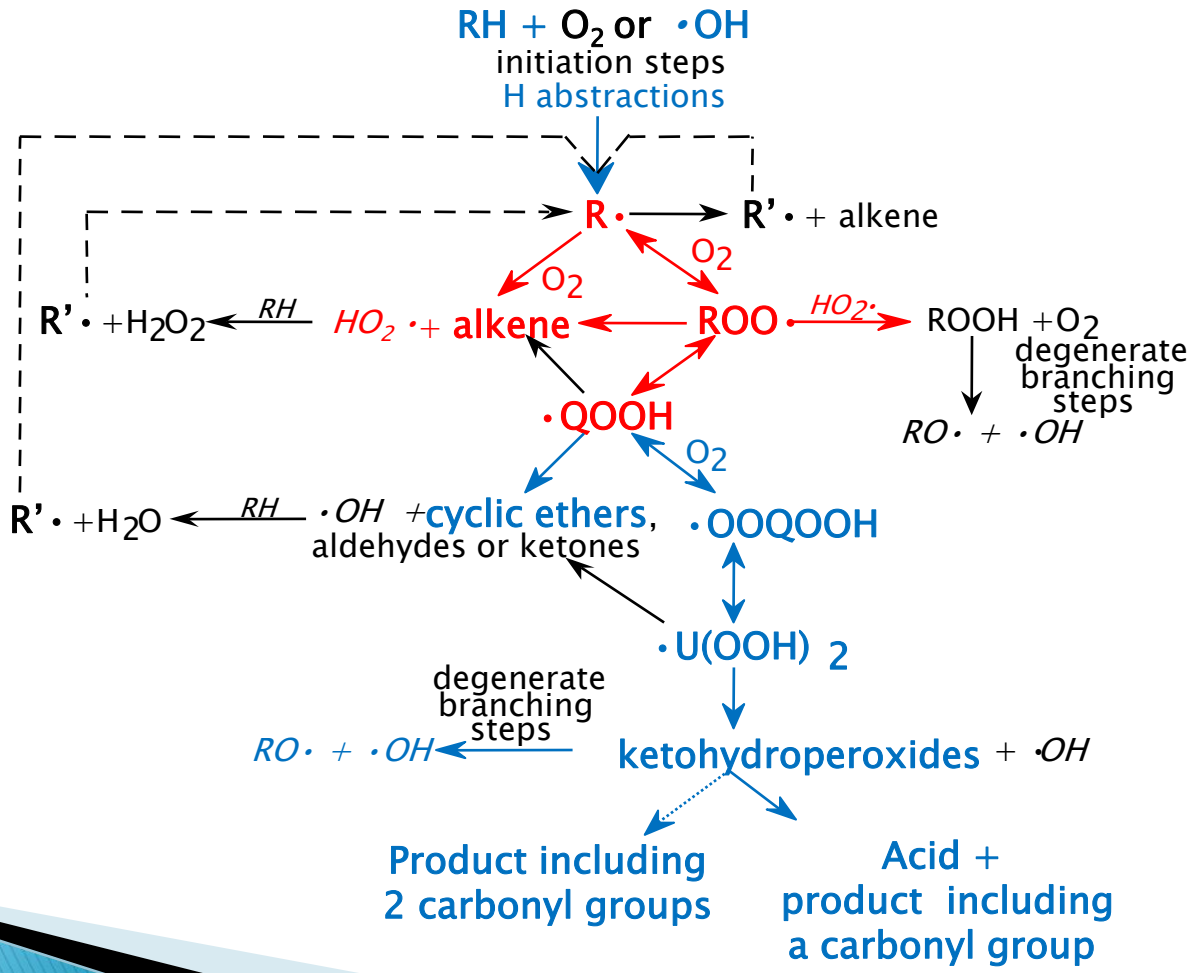


S. Som, M.J. Davis et al.,
J. Phys. Chem. Letters, 2013

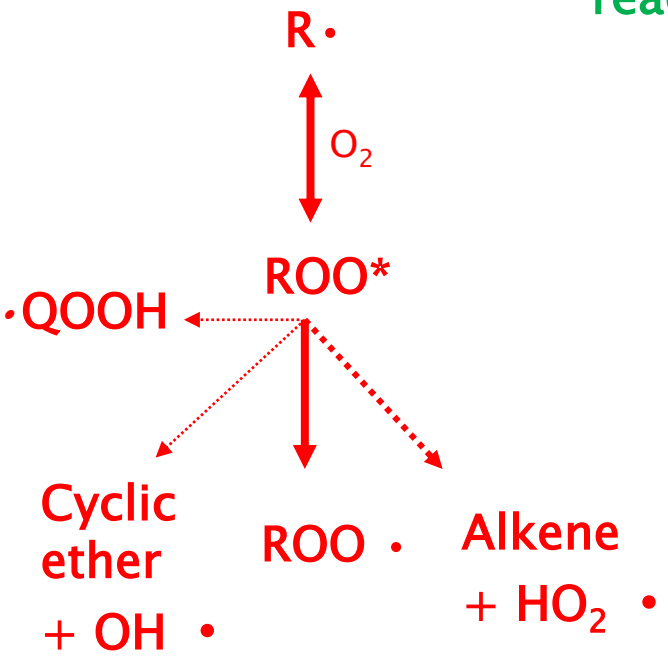
Kinetic parameters only based on theoretical studies or complex mechanism fitting

Origin of kinetics used in alkane LTO models

- **Reactions involving alkylperoxy radicals**

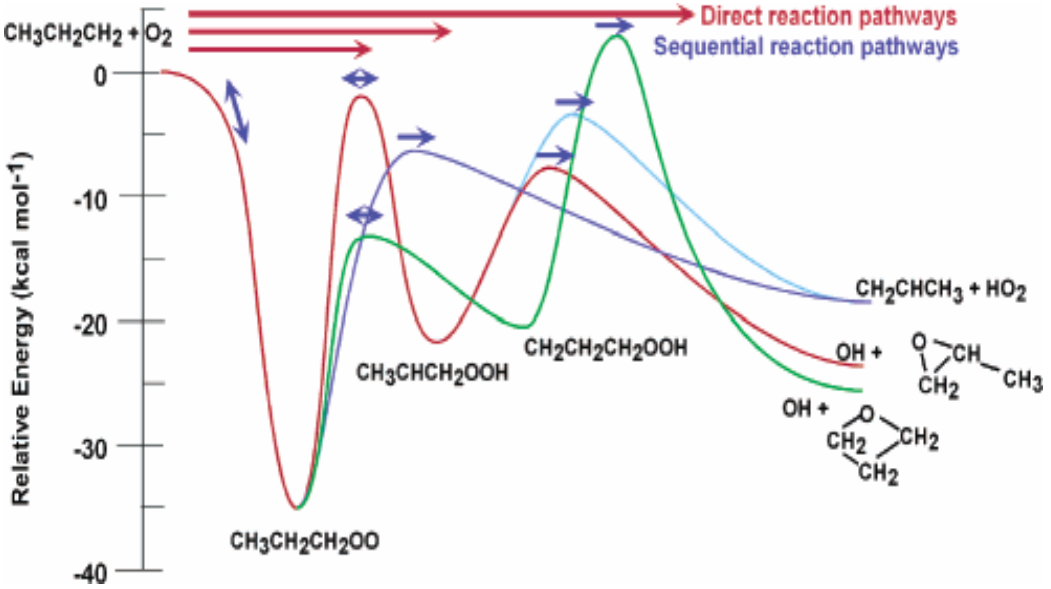


Reactions involving ROO* radicals



Schematic potential energy surfaces for the reactions of *n*–propyl radicals with oxygen molecules

J.D. DeSain, S.J. Klippenstein, J.A. Miller, C.A. Taatjes, JPCA, 2003



Rate constants need to be parametrized as a function of temperature and pressure using master equation

This should also be done for C_{3+} alkanes

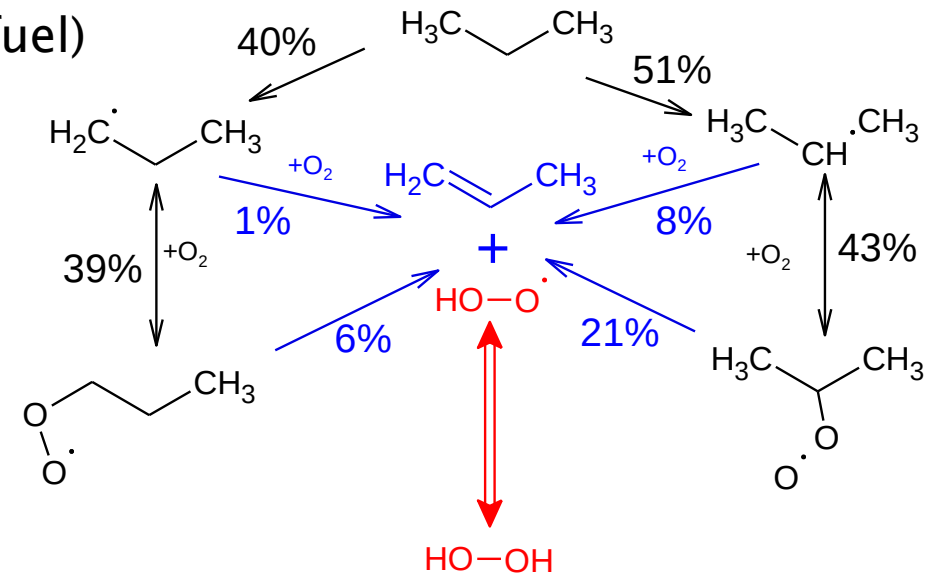
Reactions involving HO_2 radicals

Flow rate analysis for JSR propane oxidation at 630 K

Using an EXGAS model with the Desain et al.'s kinetic values

(ϕ = 1, P = 1 bar, τ = 2 s, 12 % initial fuel)

M. Cord, R. Fournet, F. Battin-Leclerc, F. Qi et al., JPCA, 2012



1/3 of propane is consumed to produce propene and HO_2 radicals

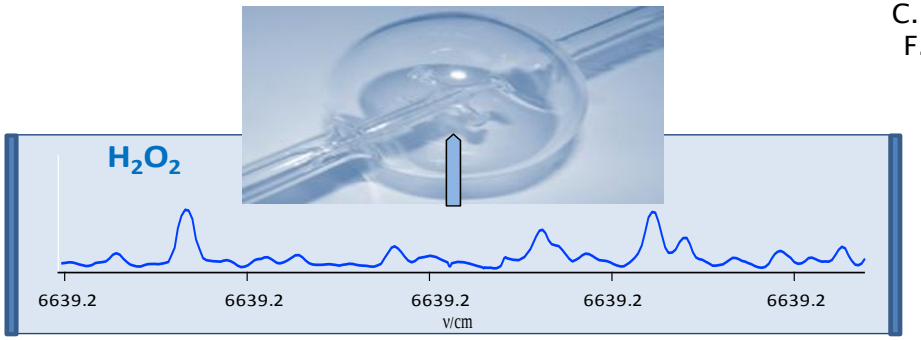
Importance of the HO_2 – H_2O_2 system

Reactions involving alkylperoxy radicals

HO_2 – H_2O_2 system

H_2O_2 and HO_2 radicals probed during *n*-butane JSR oxidation

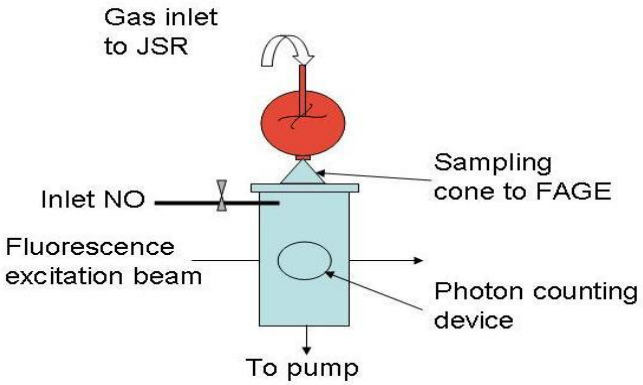
H_2O_2 and HO_2 by Cavity Ring Down Spectroscopy (CRDS)



H_2O_2
C. Bahrini, O. Herbinet, C. Fittschen, F. Battin-Leclerc, et al., JACS, 2012

H_2O_2 and HO_2 radicals
M. Djehiche, G. Dayma, P. Dagaut et al., JACS, 2014

OH and HO_2 by Fluorescence Assay Gas Expansion (FAGE)



M. Bloquet, C. Schoemaecker , O. Herbinet, F. Battin-Leclerc, C. Fittschen et al., PNAS, 2013

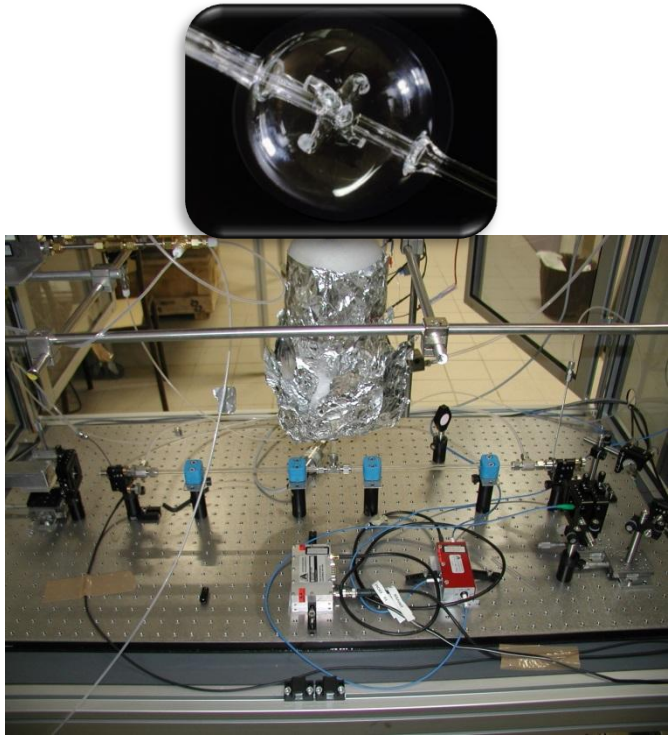
Loss of radicals when probed from JSR to an external optical cell

Reactions involving alkylperoxy radicals

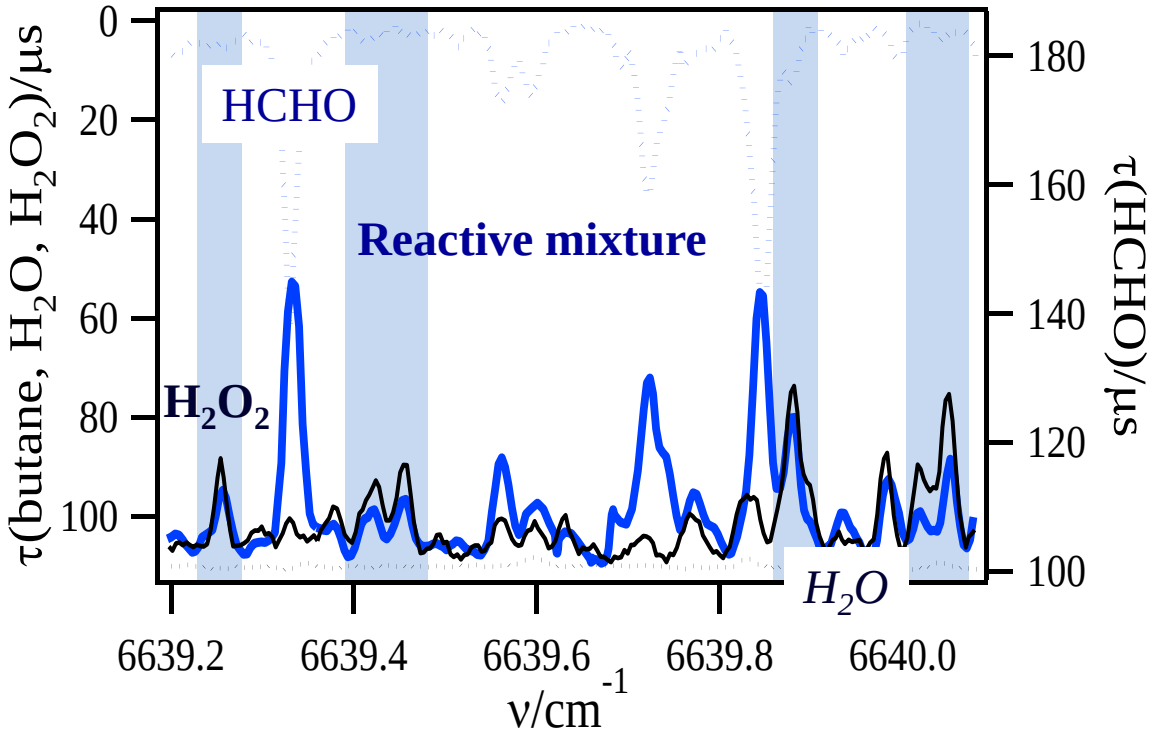
$HO_2 - H_2O_2$ system

Probing H_2O_2 by CRDS in a complex combustion mixture

JSR, P = 1 bar, Φ = 1, τ = 6 s, 2.3% *n*-butane, 650 K



C. Bahrini, O. Herbinet, C. Fittschen,
F. Battin-Leclerc, et al.,



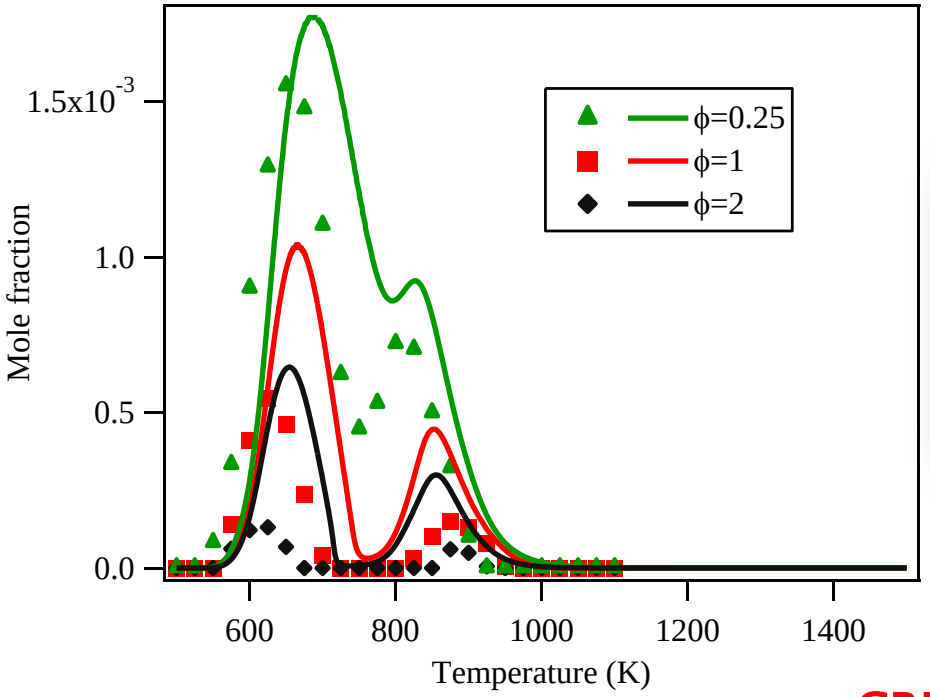
Reactions involving alkylperoxy radicals

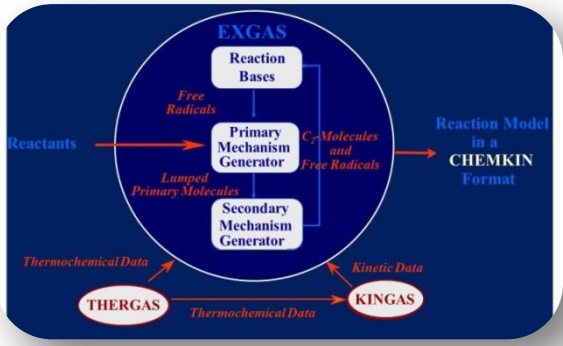
$HO_2 - H_2O_2$ system

Quantifying H_2O_2 by CRDS during JSR oxidation of *n*-heptane

Symbols correspond to GC experiments and lines to simulations
($\phi = 1$, P = 1 bar, $\tau = 2$ s, 0.5 % initial fuel,

A. Rodriguez, O. Herbinet, C. Fittschen,
F. Battin-Leclerc, unpublished results, 2015





CRDS can probe H_2O_2
even for current fuel surrogates

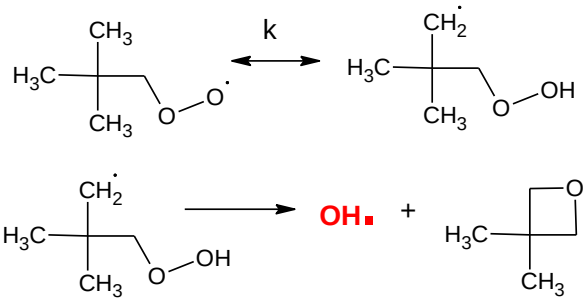
Reactions involving alkylperoxy radicals

Isomerizations of ROO radicals

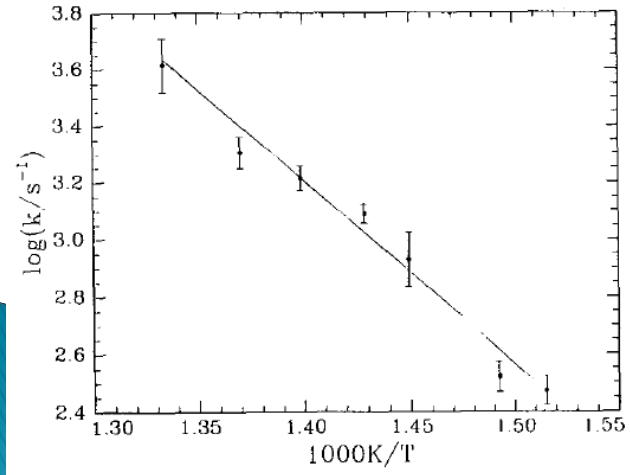
Direct experimental determination

Laser flash photolysis of neo-$C_5H_{11}I$ in O_2/He with OH LIF detection, 660–750 K

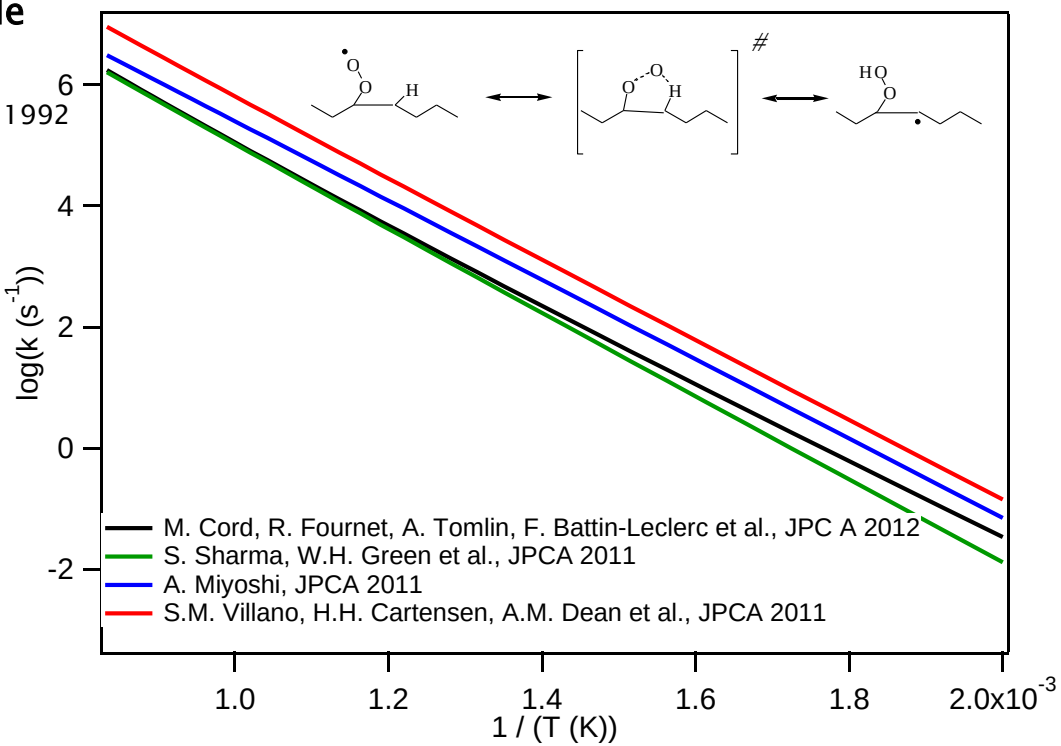
K.J. Hughes, T. Turányi, M.J. Pilling, et al. Proc. Combust. Inst. 1992



$k = 10^{12.2}\exp(14800/T)\ s^{-1}$



Theoretical calculations



Deviations betwen values calculated by the different groups up to a factor of 4

Need to detect ephemeral QOOH radicals

A first success from 1,3-cycloheptadiene

J.D. Savee, C. Taatjes et al., Science, 2015

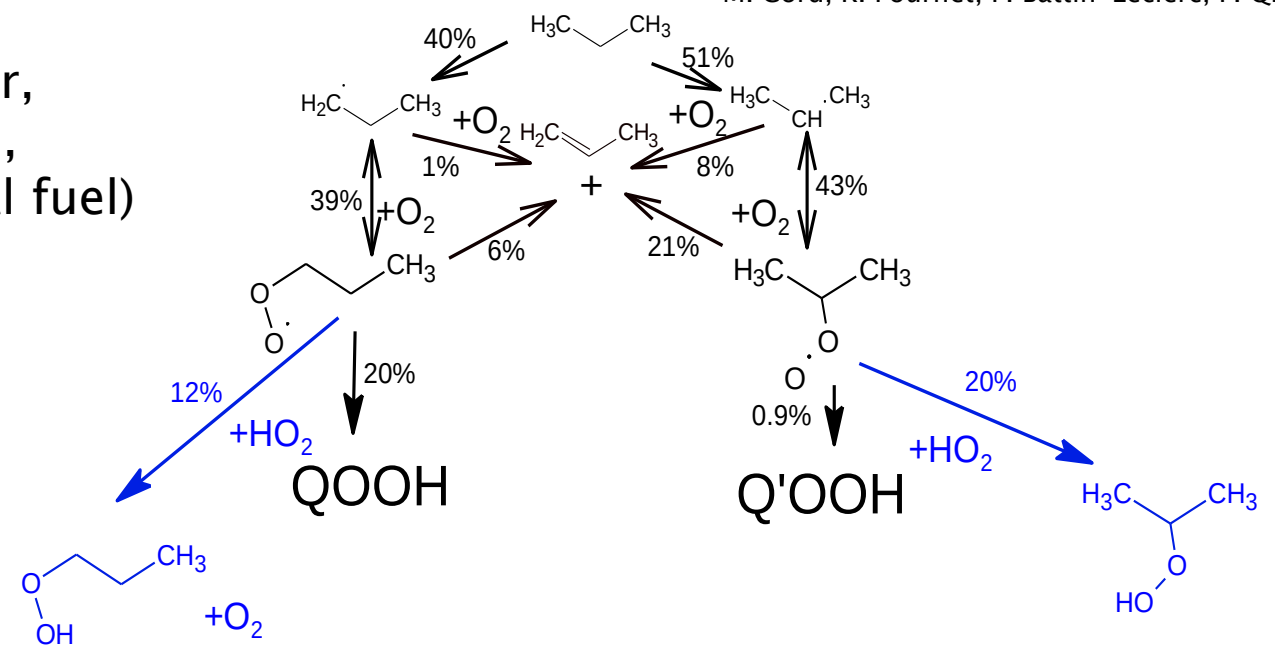
Reactions of ROO radicals with other radicals

Flow rate analysis for JSR propane oxidation at 630 K

Using an EXGAS model with the theoretical calculated rate constants for isomerizations

M. Cord, R. Fournet, F. Battin-Leclerc, F. Qi et al., JPC A, 2012

(ϕ = 1,
P = 1 bar,
τ = 2 s,
τ 12 % initial fuel)



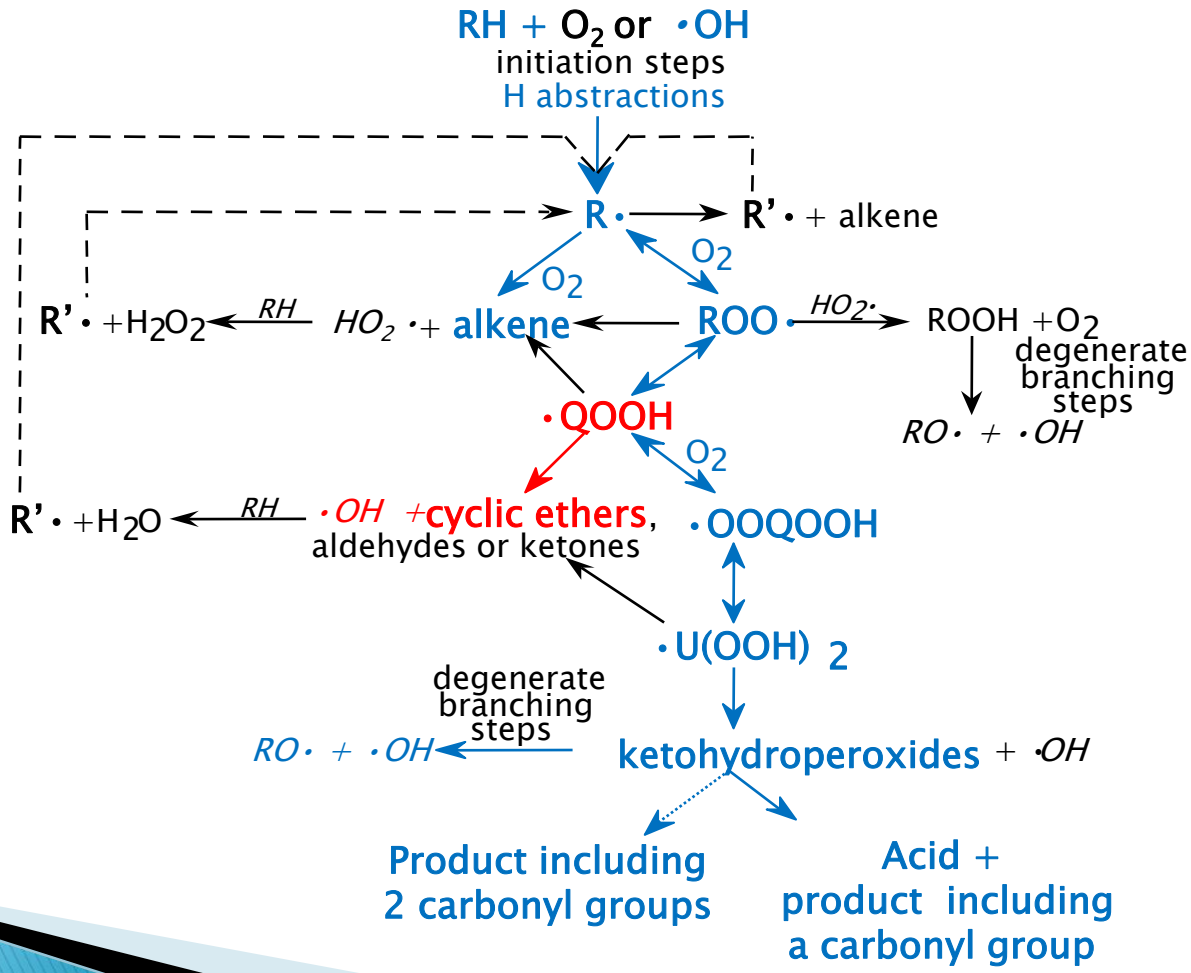
1/3 of propane is consumed by reactions of peroxy and HO_2 radicals

Very few rate constants available above room temperature and for C_{3+} compounds

T.J. Wallington, P. Dagaut, M.J. Kutylo, Chem. Rev. 1992
J.J. Orlando and G.S. Tyndall, Chem. Soc. Rev. 2012

Origin of kinetics used in alkane LTO models

- **Formation of cyclic ethers**



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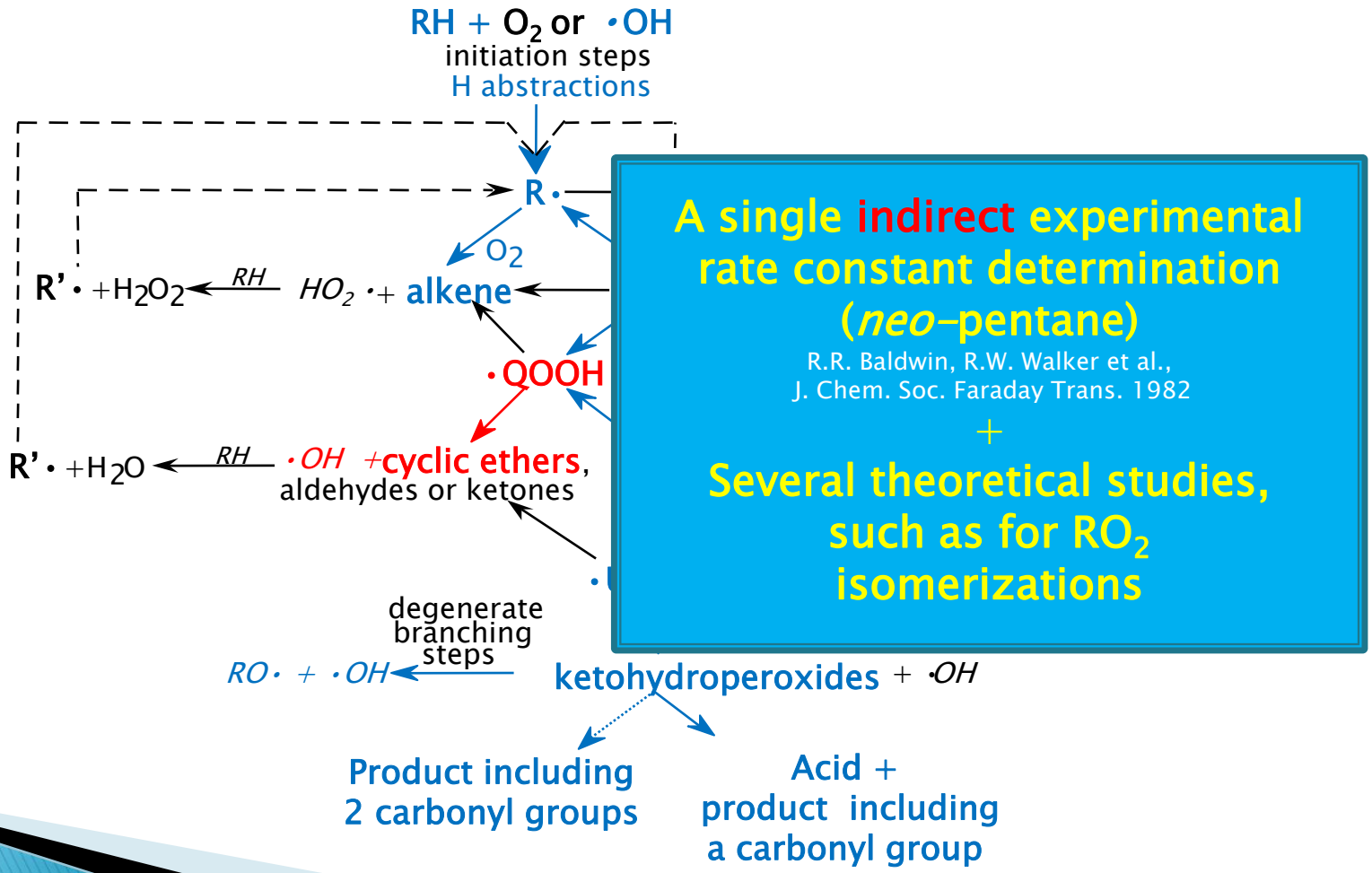
- **Formation of cyclic ethers**

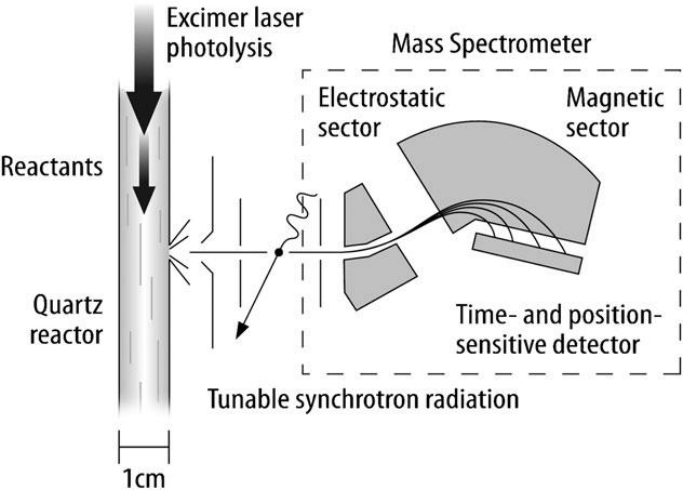


Formation of cyclic ethers

- Detection of cyclic ether in photolytically initiated alkane oxidation

Mass spectrometry combined with tunable synchrotron vacuum ultraviolet photoionization

C.A. Taatjes, N. Hansen,
D. Osborn, T. Cool et al. PCCP, 2008



Time of flight MS

Laser flash photolysis formation of Cl atoms which react with a $RH/O_2/He$ mixture slowly flowing in a quartz tube of 1.05 cm diameter

By courtessy of C.A. Taatjes

Berkeley Advanced light source

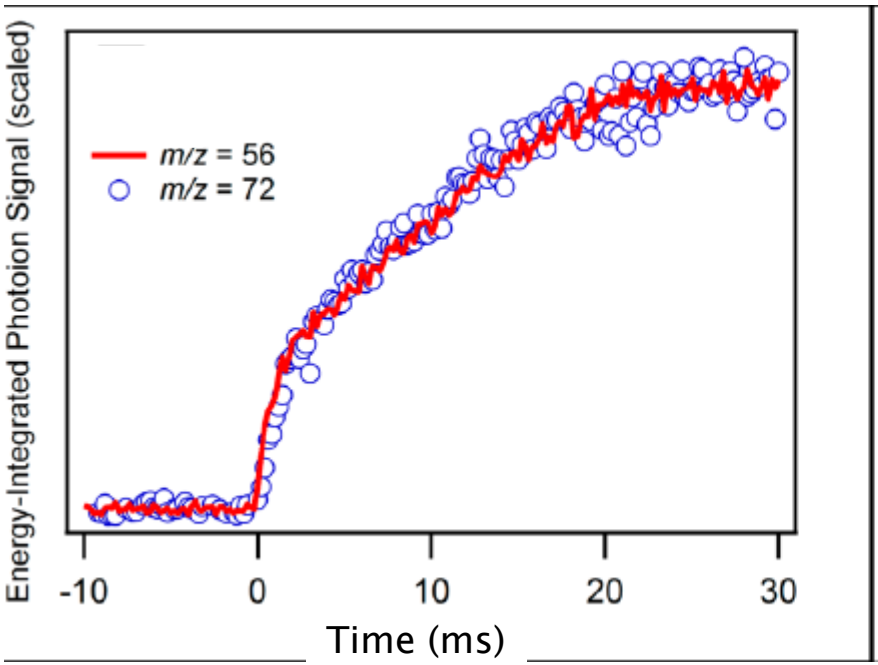
Formation of cyclic ethers

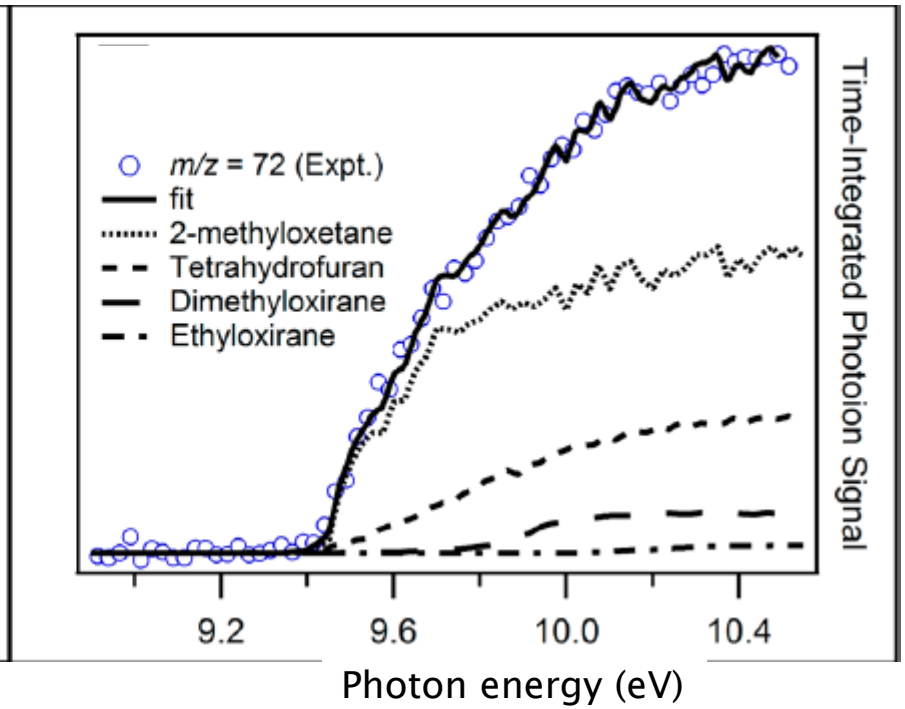
- Detection of cyclic ether in photolytically initiated alkane oxidation

Mass spectrometry combined with tunable synchrotron vacuum ultraviolet photoionization to study *n*–butane oxidation

A.J. Eskola, D. Osborn, C.A. Taatjes et al., JPCA 2008

Time behaviors and photoionization spectra of cyclic ethers at 575 K, 4 Torr

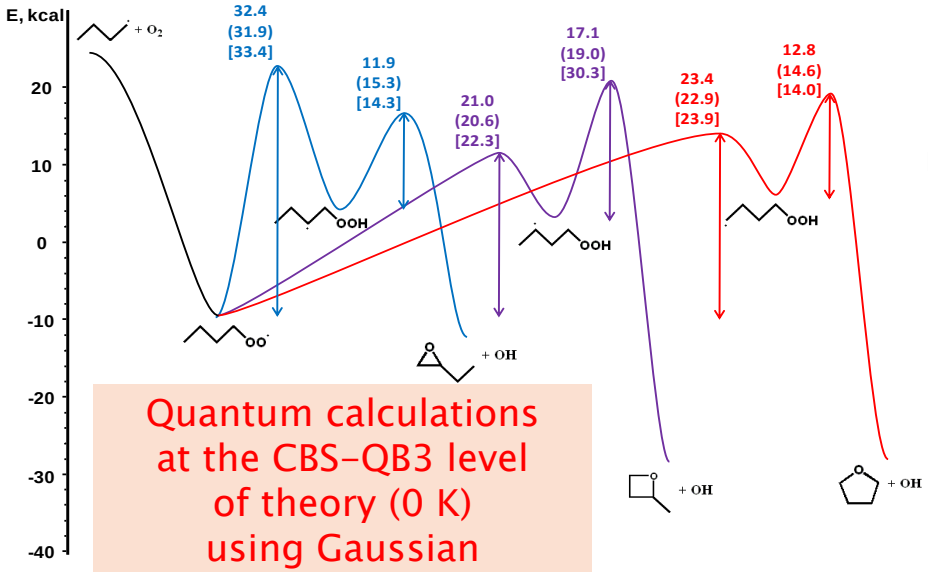




A good source of data to confirm the theoretically calculated rate constants

Formation of cyclic ethers

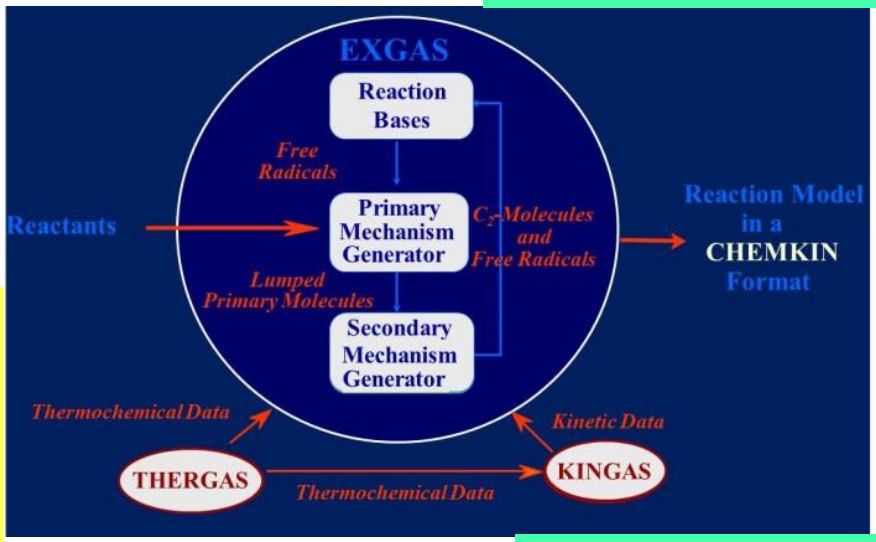
- **Modeling the formation of cyclic ethers during JSR alkane oxidation**
  Inclusion of theoretically calculated rate constants in automatically generated models



Quantum calculations at the CBS-QB3 level of theory (0 K) using Gaussian

M. Cord, R. Fournet, A. Tomlin, F. Battin-Leclerc et al., JPCA 2012

Thermodynamic data also revised from theoretical calculations



High pressure limit rate constants calculated using transition state theory for C_4 alkanes
+
New C_{4+} kinetic correlations for isomerizations and cyclic ether formations

Rate constants of the $R+O_2$ system taken from DeSain et al. 2003

Formation of cyclic ethers

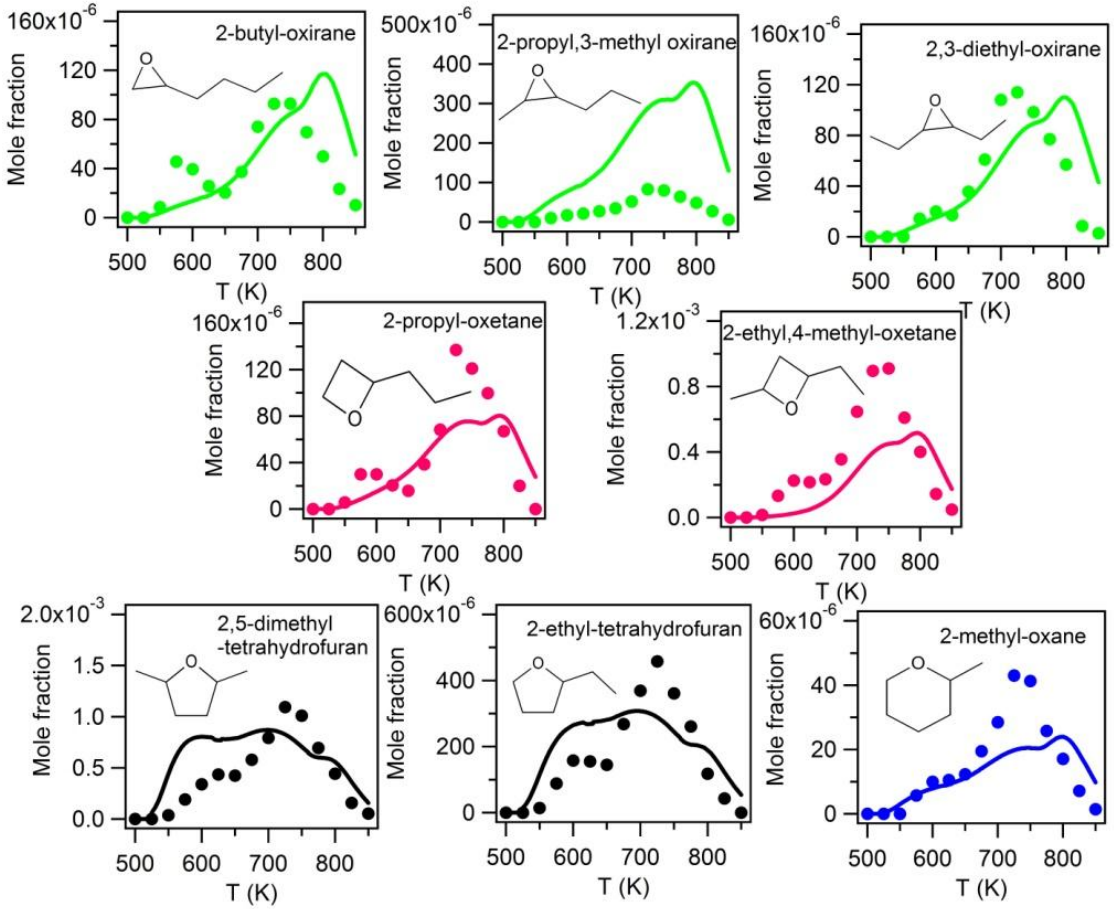
- **Modeling the formation of cyclic ethers during JSR alkane oxidation**

Oxidation of *n*-hexane

Symbols correspond to experiments and lines to simulations

(ϕ = 1, P = 1 bar, τ = 2 s, 2 % initial fuel)

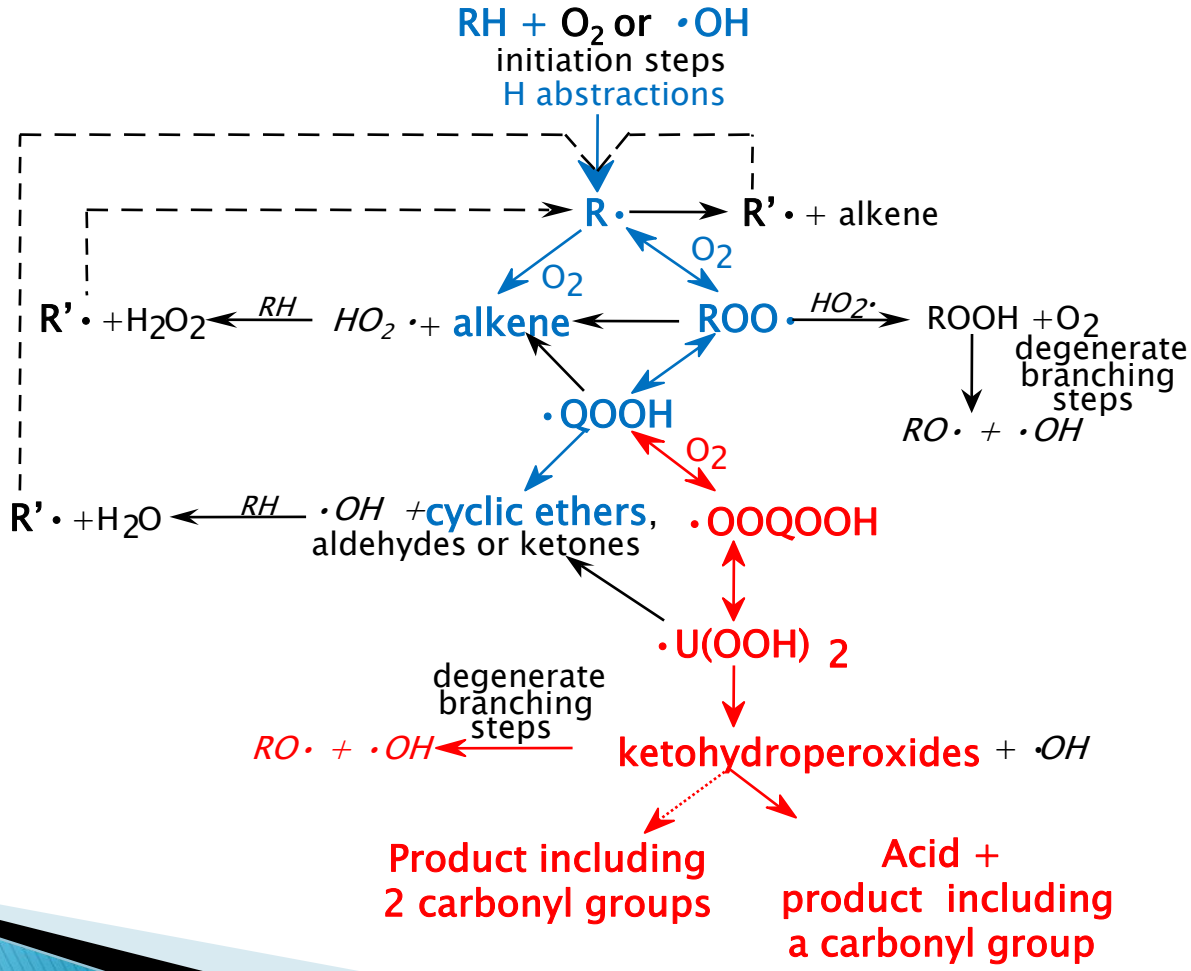
Z. Serinyel, O. Herbinet, V. Warth, F. Battin-Leclerc et al. 8th meditereanean meeting 2013



The prediction of cyclic ethers is well improved

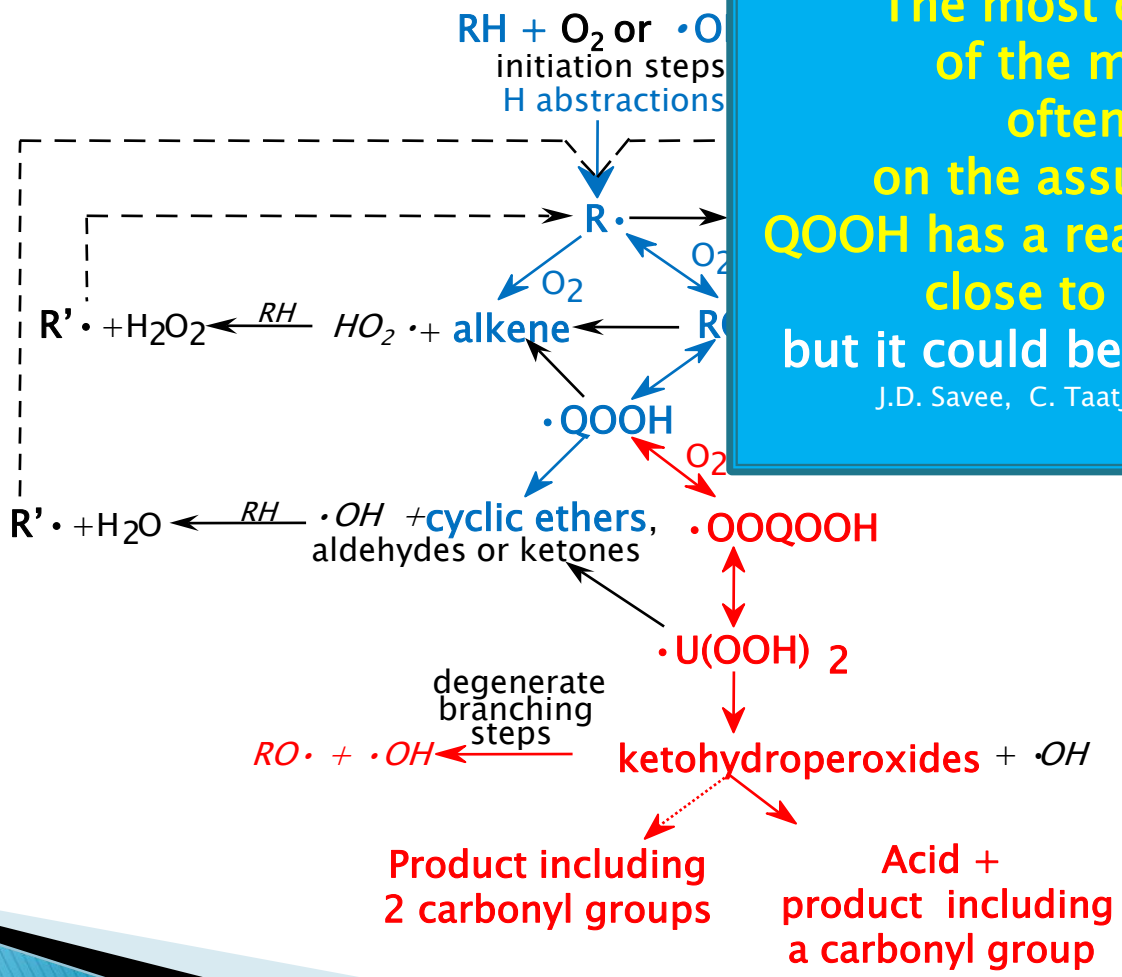
Origin of kinetics used in alkane LTO models

- **Reactions producing and consuming ketohydroperoxides**



Origin of kinetics used in alkane LTO models

- **Reactions producing and consuming ketohydroperoxides**



The most obscure part
of the mechanism
often based
on the assumption that
QOOH has a reactivity toward O_2
close to R radicals,
but it could be 10 times higher

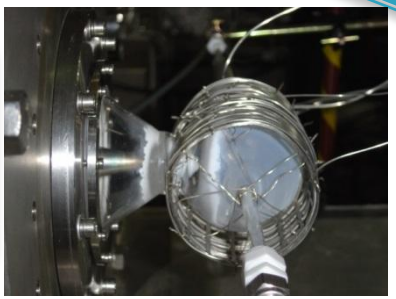
J.D. Savee, C. Taatjes et al. Science 2015

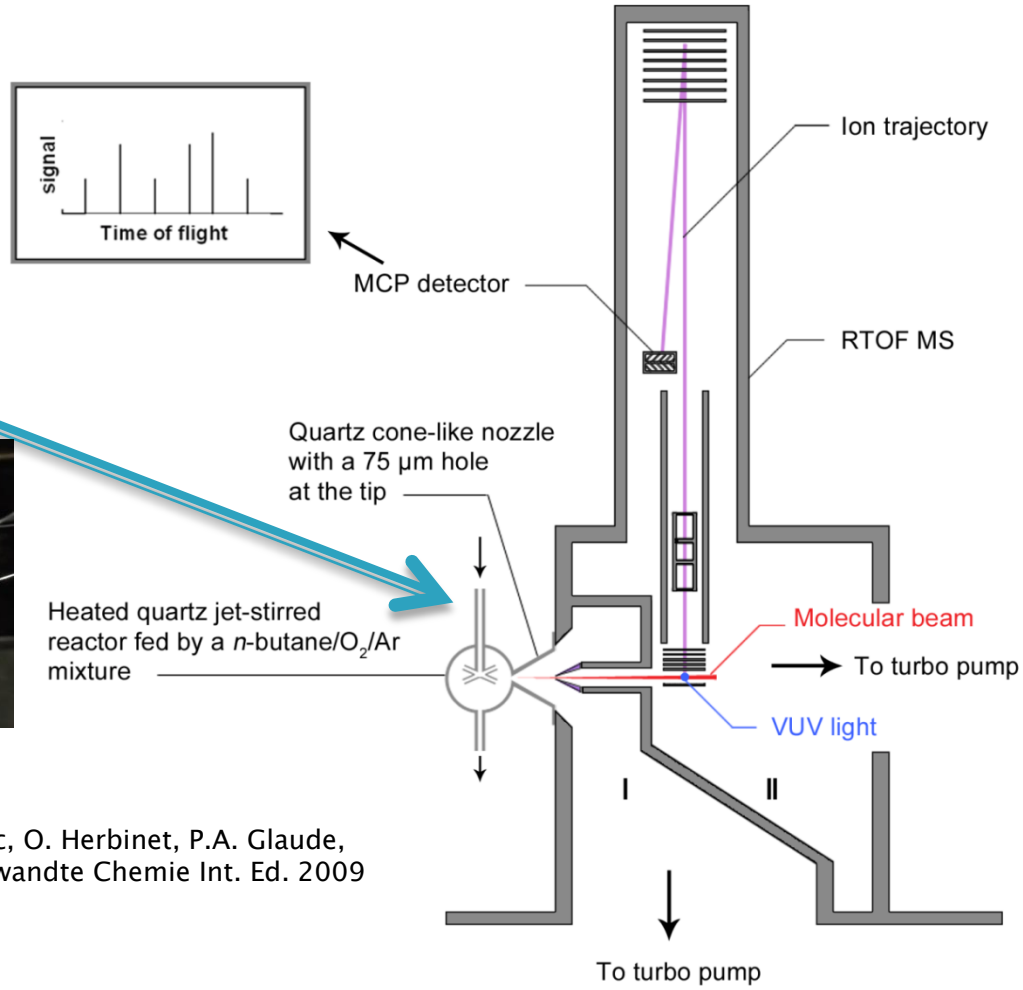
Reactions producing and consuming ketohydroperoxides

Ketohydroperoxide detection only recently

Coupling of a mass spectrometer combined with tunable synchrotron vacuum ultraviolet photoionization (PI-MS) to a JSR through a molecular-beam sampling system

Isotherm quartz jet-stirred reactor at atmospheric pressure (JSR)





F. Battin-Leclerc, O. Herbinet, P.A. Glaude, F. Qi et al. Angewandte Chemie Int. Ed. 2009

Reactions producing and consuming ketohydroperoxides

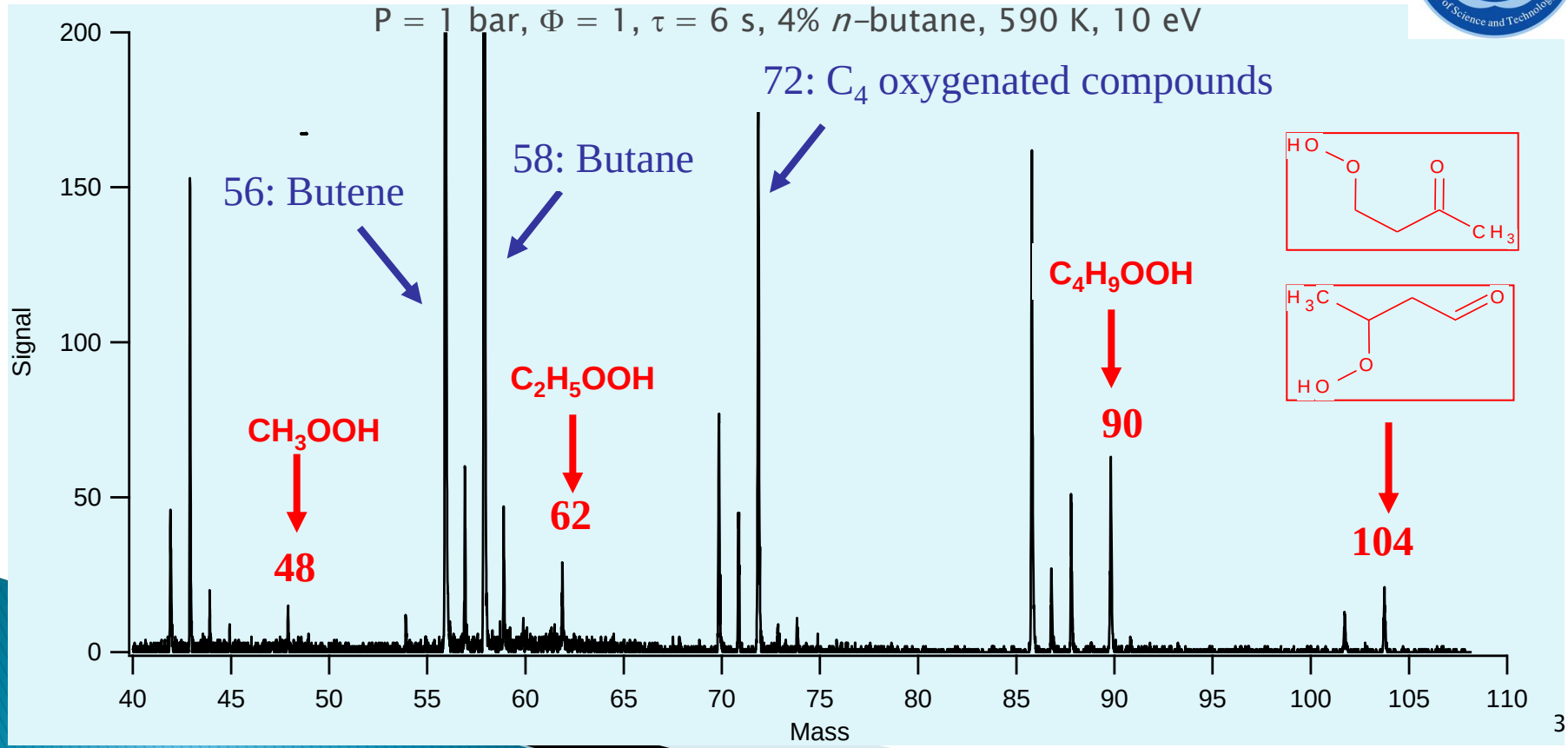
- **Ketohydroperoxide detection only recently**

Coupling of PI-MS to a JSR through a molecular-beam sampling system

Study of the low-temperature oxidation of alkanes: *n*-butane

F. Battin-Leclerc, O. Herbinet, P.A. Glaude, F. Qi et al. Angewandte Chemie Int. Ed. 2009

Obtained mass spectrum



Reactions producing and consuming ketohydroperoxides

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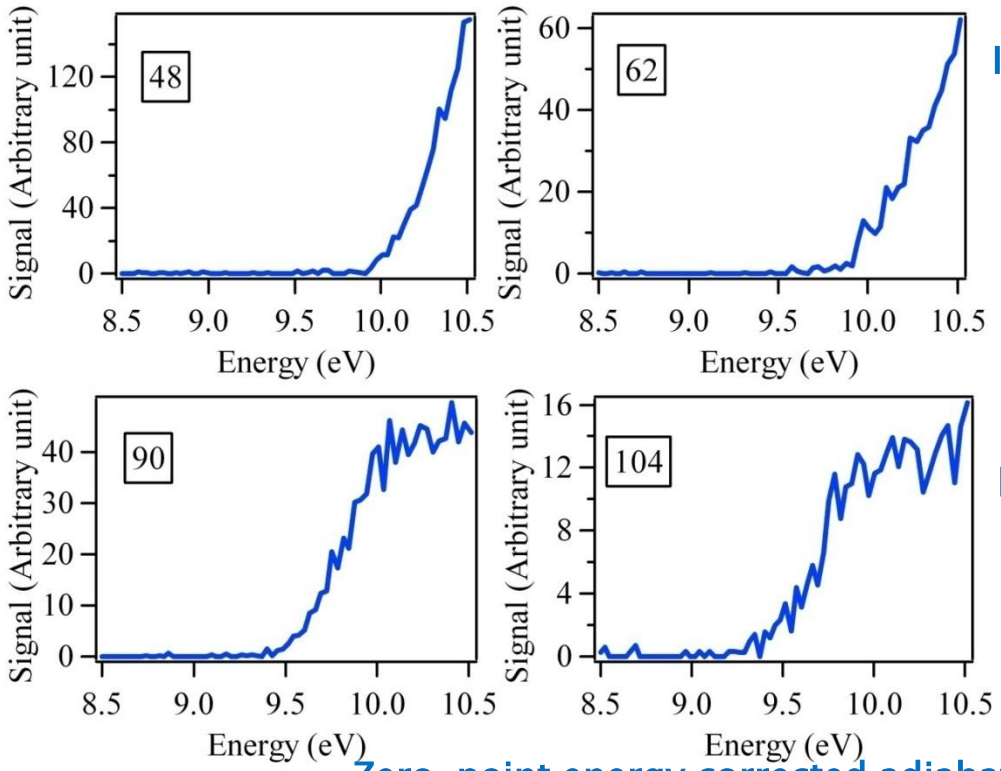
Study of the low-temperature oxidation of alkanes: *n*-butane

F. Battin-Leclerc, O. Herbinet, P.A. Glaude, F. Qi et al. Angewandte Chemie Int. Ed. 2009

Ionization energy (IE) measurements

P = 1 bar, Φ = 1, τ = 6 s, 4% *n*-butane, 590 K, 10 eV

IE of CH_3OOH = 9.83 eV



IE of C_2H_5OOH = 9.61 eV

IE of C_4H_9OOH = 9.33-9.36 eV

IE of ketohydroperoxides = 9.34-9.39 eV

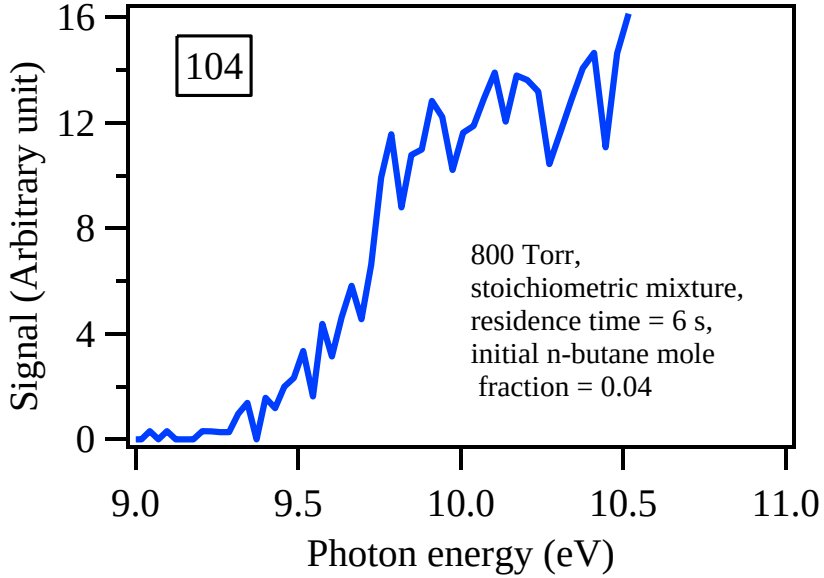
Zero-point energy corrected adiabatic IEs have been calculated from the CBS-QB3 method using Gaussian03.

Reactions producing and consuming ketohydroperoxides

- **Ketohydroperoxide detection only recently**

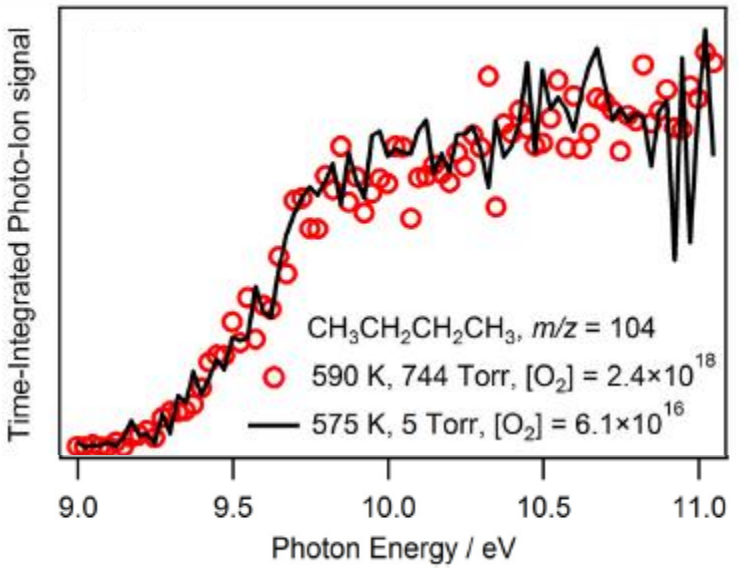
Comparison between ketohydroperoxide photoionization spectrum obtained during n-butane oxidation in a JSR and in a photolysis tube

Jet-stirred reactor (this study)



F. Battin-Leclerc, O. Herbinet, P.A. Glaude, F. Qi et al. Angewandte Chemie Int. Ed. 2009

Pulsed photolysis experiments ($RH + Cl. + O_2$)



A.J. Eskola, C.A. Taatjes et al., Proc; Combust. Inst. 2015

Both spectra are similar, showing that the same isomer is formed in thermal or photolysis experiments whatever the pressure

Reactions producing and consuming ketohydroperoxides

Ketohydroperoxide detection only recently

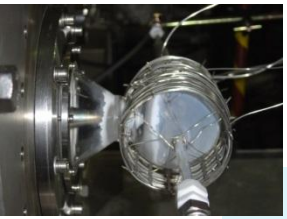
Formation of hydroperoxides according to alkanes studied in JSR

Fuel	Alkyl hydroperoxides	Keto hydroperoxides
Propane M. Cord, R. Fournet, F. Battin-Leclerc, F. Qi et al. JPCA 2012	Yes	No
n-butane F. Battin-Leclerc, O. Herbinet, P.A. Glaude, F. Qi et al. Angewandte Chemie Int. Ed. 2009	yes	yes
n-pentane O. Herbinet, F. Battin-Leclerc, F. Qi et al. unpublished results,2015	yes	Yes
Hexane isomers Z. Wang, O. Herbinet, F. Battin-Leclerc, F. Qi et al. JPCA 2014	No	Yes
n-heptane O. Herbinet, Z. Serinyel, V. Warth, F. Battin-Leclerc, F. Qi et al. Combust. Flame 2012	No	Yes

Reactions producing and consuming ketohydroperoxides

Ketohydroperoxide detection only recently

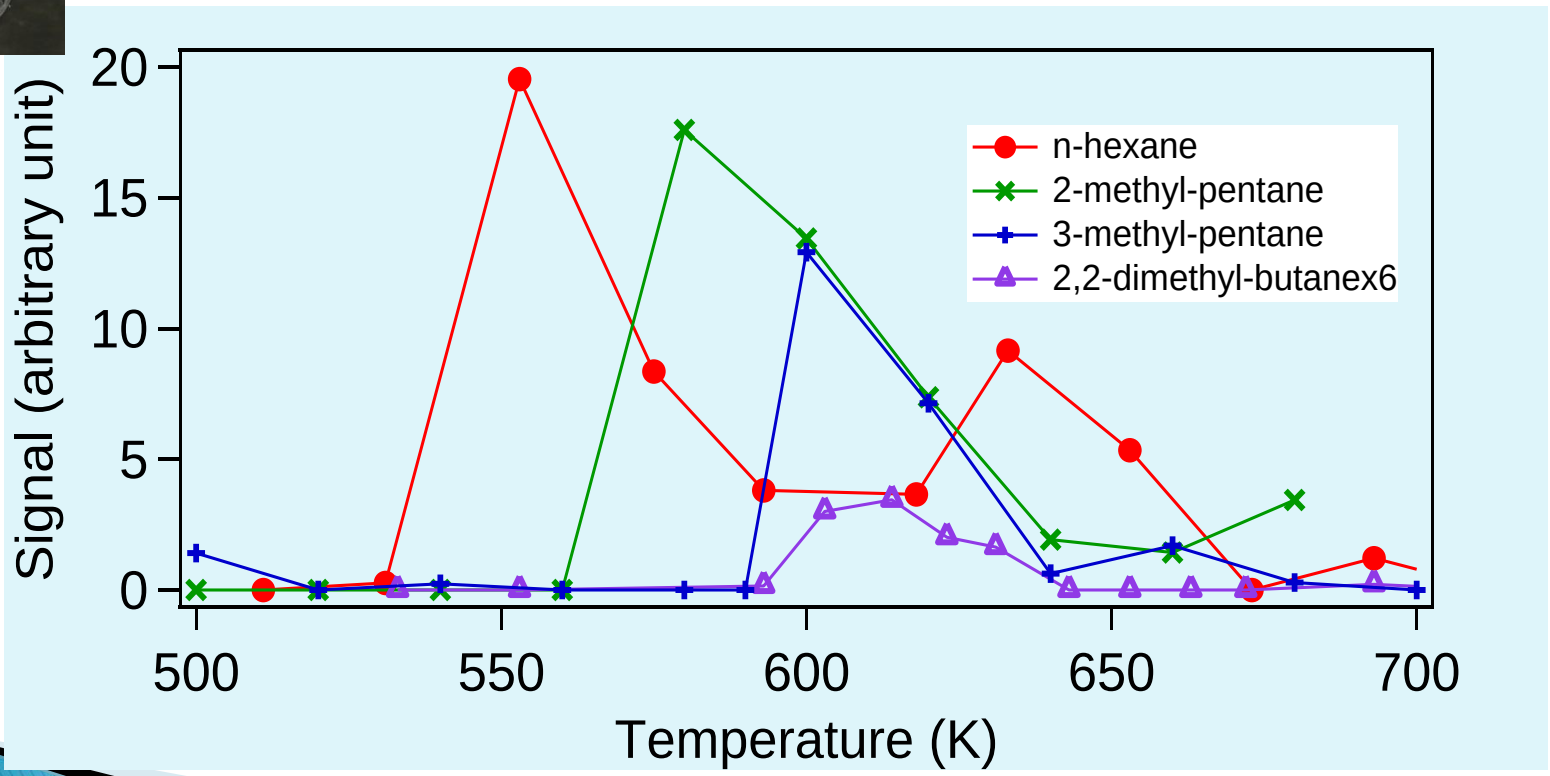
Formation of ketohydroperoxides from linear and branched hexanes in JSR



Ketohydroperoxide signal evolution with temperature

P = 1 bar, Φ = 1, τ = 2 s, m/z = 132, ionization energy = 10.5 eV

Z. Wang, O. Herbinet, F. Battin-Leclerc, F. Qi et al. JPCA 2014



The more branched the isomer, the higher the temperature of appearance of ketohydroperoxides

Reactions producing and consuming ketohydroperoxides

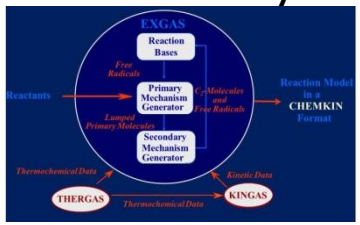
Hydroperoxide quantification

O. herbinet,
F. Battin-leclerc et al. PCCP 2011

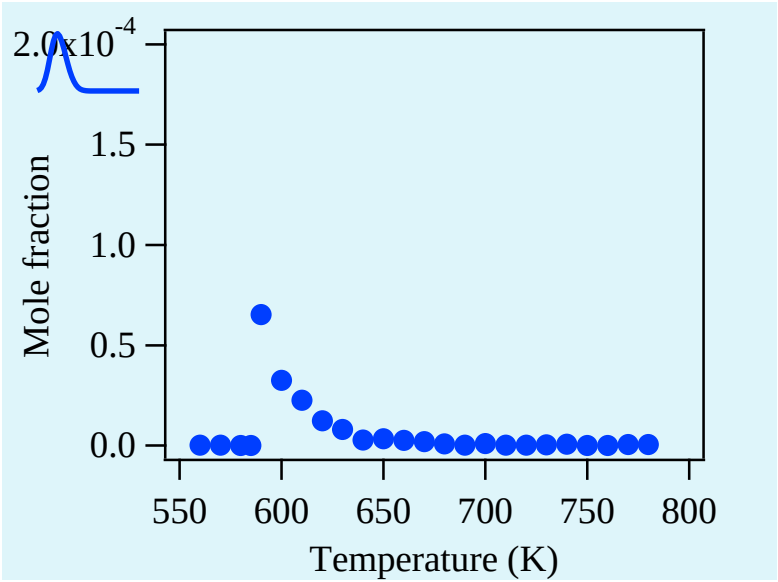
Quantification of C_4 hydroperoxides

Symbols correspond to experiments and lines to simulations

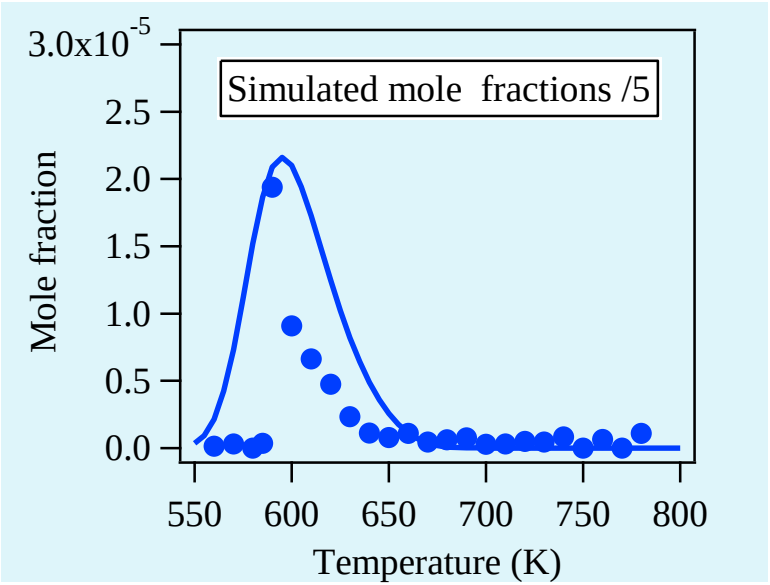
P = 1 bar, Φ = 1, τ = 6 s, 4% *n*-butane



C_4H_9OOH



Ketohydroperoxides



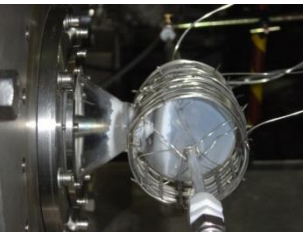
$$\frac{S_i(T)}{S_{ref}(T)} = \frac{X_i(T)}{X_{ref}(T)} \cdot \frac{\sigma_i(T)}{\sigma_{ref}(T)} \cdot \frac{D_i(T)}{D_{ref}(T)}$$

Calibrated from butene GC measurements with σ_i taken as equal to that of tetrahydrofuran

Reactions producing and consuming ketohydroperoxides

- **Ketohydroperoxide consumption not only yields alkoxy and OH radicals**

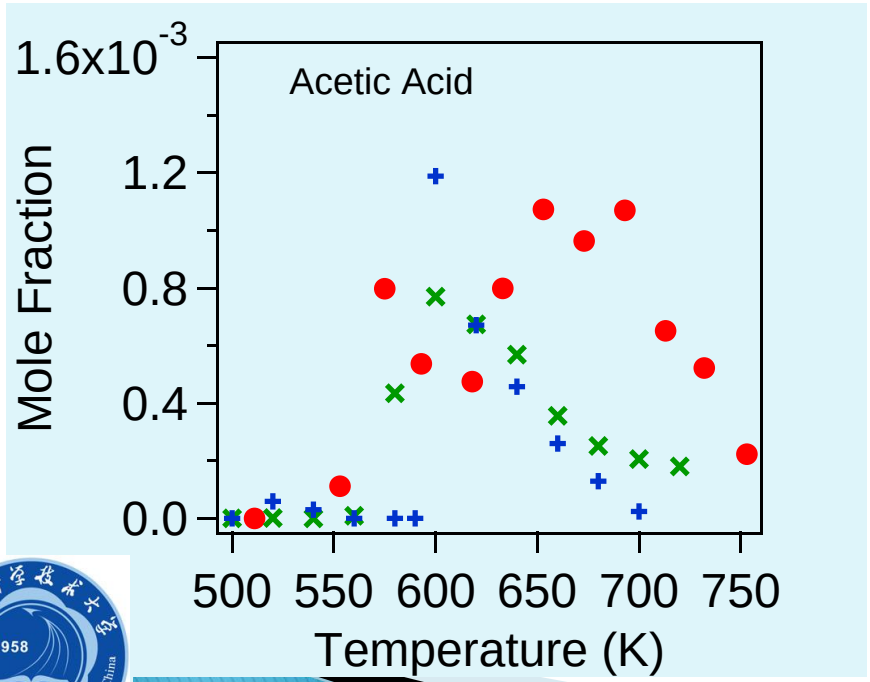
Z. Wang, O. Herbinet, F. Battin-Leclerc, F. Qi et al. JPC A 2014

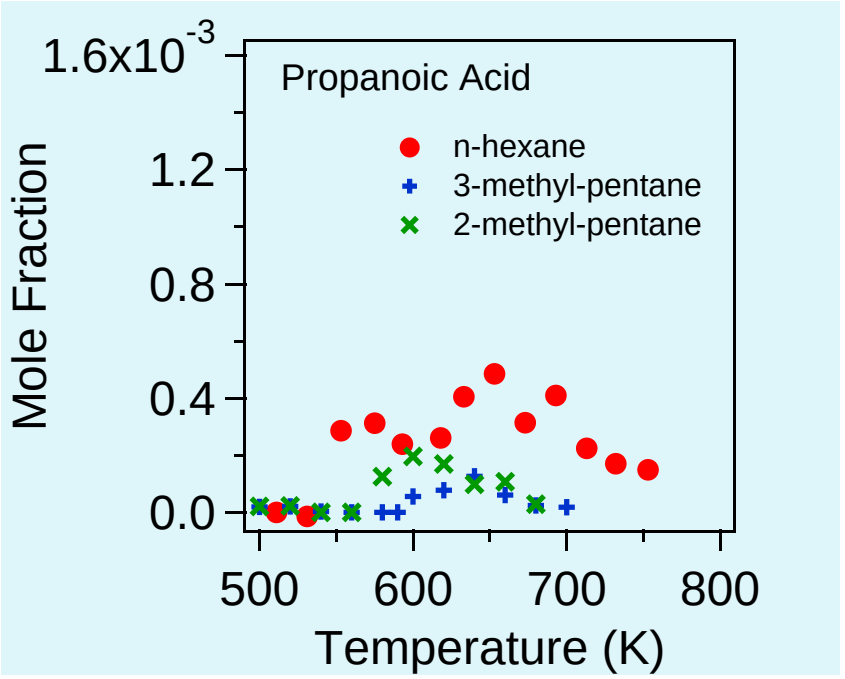


Formation of carboxylic acids

Acid mole fraction evolution with temperature during hexane isomer JSR oxidation

P = 1 bar, Φ = 1, τ = 2 s, PI-MS

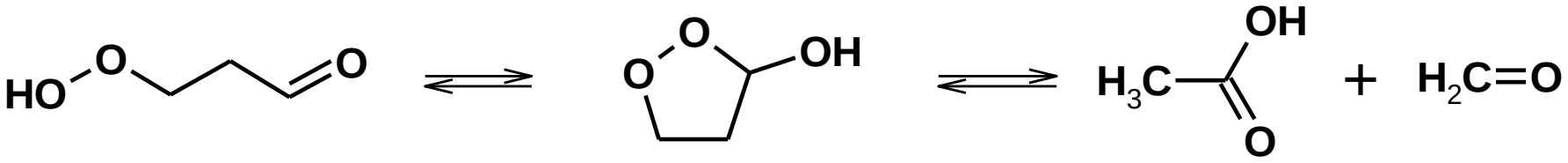




Reactions producing and consuming ketohydroperoxides

- **Ketohydroperoxide consumption not only yields alkoxy and OH radicals**

Formation of acetic acid from ketohydroperoxides



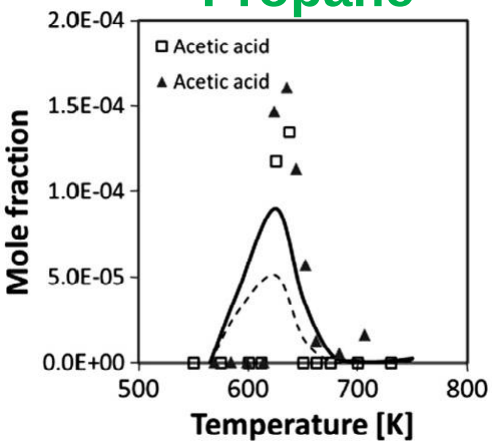
A. Jalan, D.G. Truhlar, W.H. Green et al. JACS 2013

Modeling acetic acid formation from Nancy JSR alkane oxidation

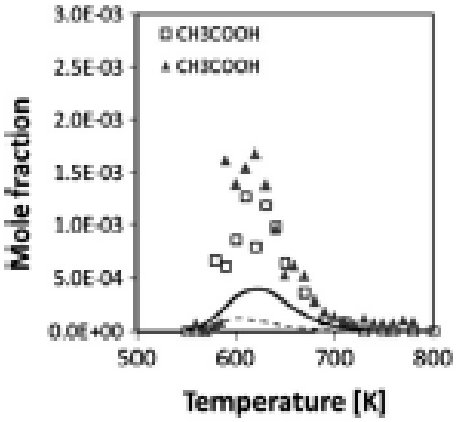
Symbols correspond to experiments and lines to simulations

P = 1 bar, Φ = 1, τ = 6 or 2 s, GC and PI-MS results

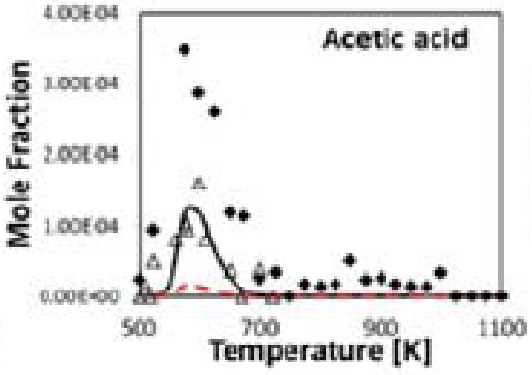
Propane



n-butane



n-heptane



E. Ranzi, T. Faravelli et al. Combust. Flame 2015

M. Pelucchi, E. Ranzi et al. Energy&Fuel 2014

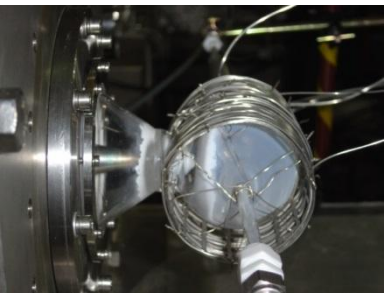
Reactions producing and consuming ketohydroperoxides

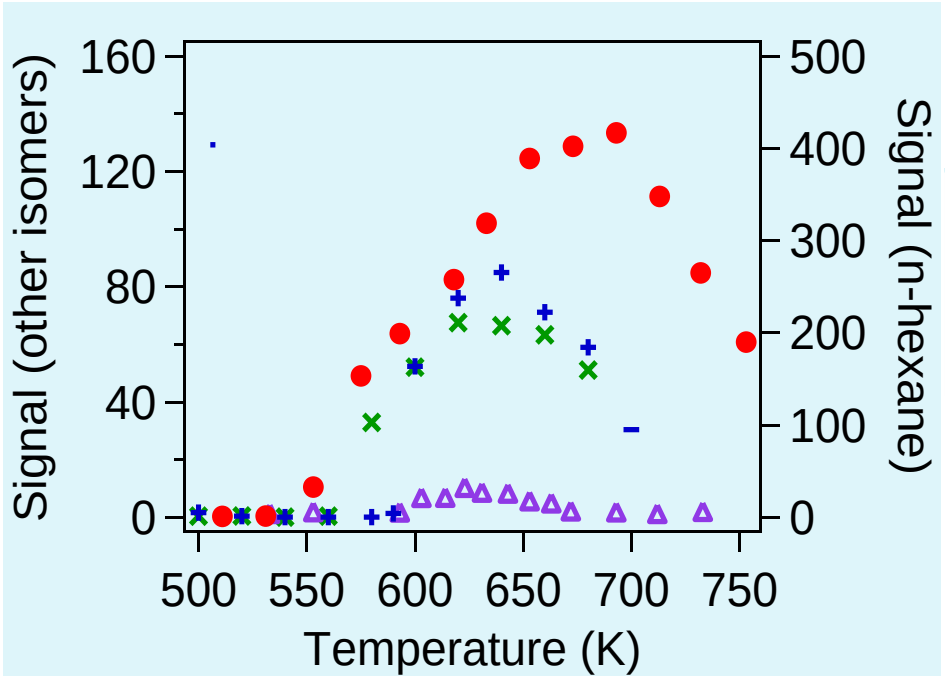
- **Ketohydroperoxide consumption not only yields alkoxy and OH radicals**

Formation of diones

Evolution with temperature of the signal at m/z = 114 during hexane isomer JSR oxidation

P = 1 bar, Φ = 1, τ = 2 s, PI-MS at 10.5 eV





Z. Wang, O. Herbinet, F. Battin-Leclerc, F. Qi et al. JPC A 2014

Reactions producing and consuming ketohydroperoxides

- **Ketohydroperoxide consumption not only yields alkoxy and OH radicals**

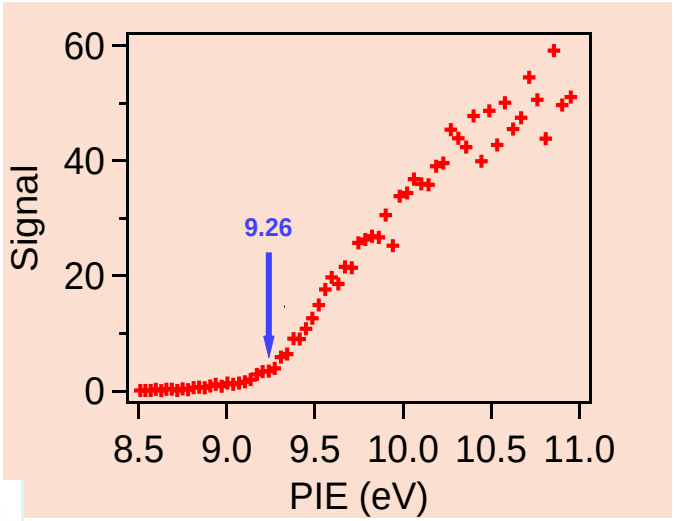
Z. Wang, O. Herbinet, F. Battin-Leclerc, F. Qi et al. JPC A 2014

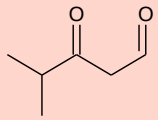
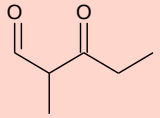
Formation of diones

Evolution with temperature of the signal at m/z = 114 during hexane isomer JSR oxidation

P = 1 bar, Φ = 1, τ = 2 s, PI-MS at 10.5 eV

Ionization energy measurement for 2-methylpentane



Name of most probable diones	Structure	Calculated ionization energy (eV) (CBS-QB3 method)
4-methyl-3-oxo-pentanal		9.26
2-methyl-3-oxo-pentanal		9.26

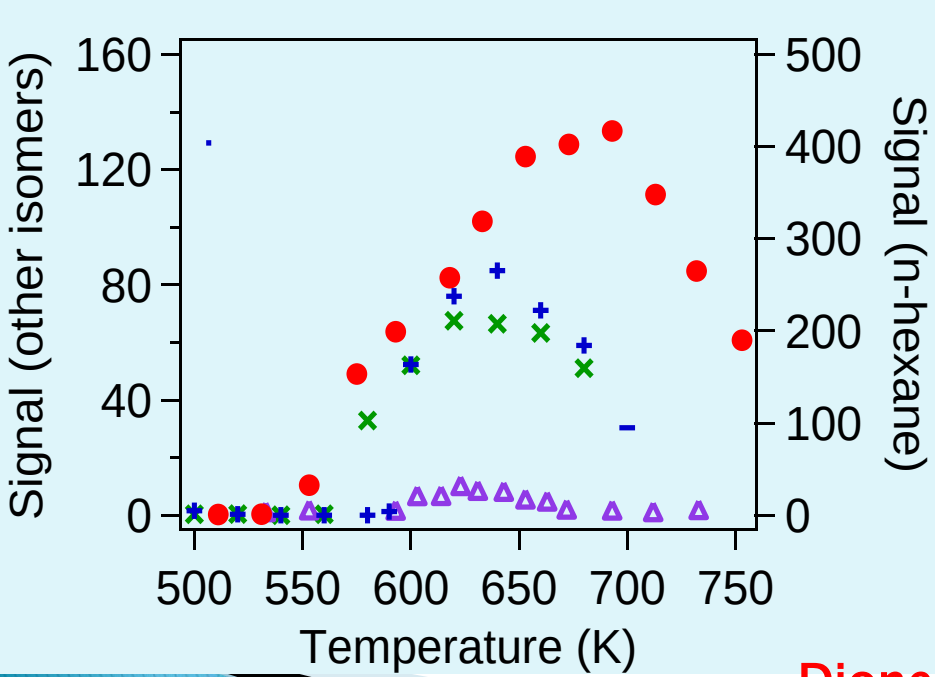
Reactions producing and consuming ketohydroperoxides

- **Ketohydroperoxide consumption not only yields alkoxy and OH radicals**

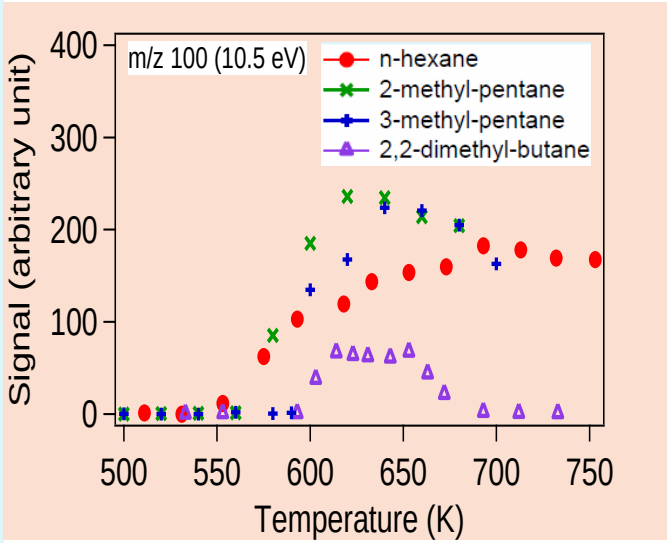
Z. Wang, O. Herbinet, F. Battin-Leclerc, F. Qi et al. JPC A 2014

Formation of diones

Evolution with temperature of the signal at m/z = 114
During hexane isomer JSR oxidation
P = 1 bar, Φ = 1, τ = 2 s, PI-MS at 10.5 eV



Signal of sum of $C_6H_{12}O$ species

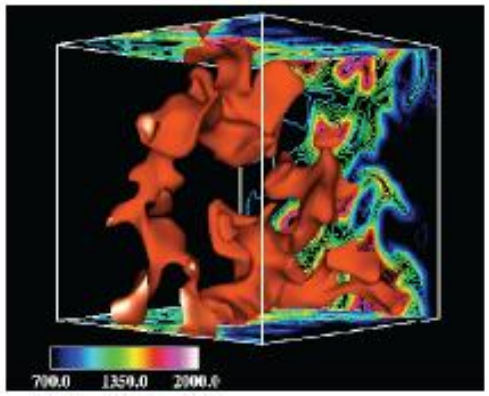


Diones: an important type of products not yet satisfactorily modeled

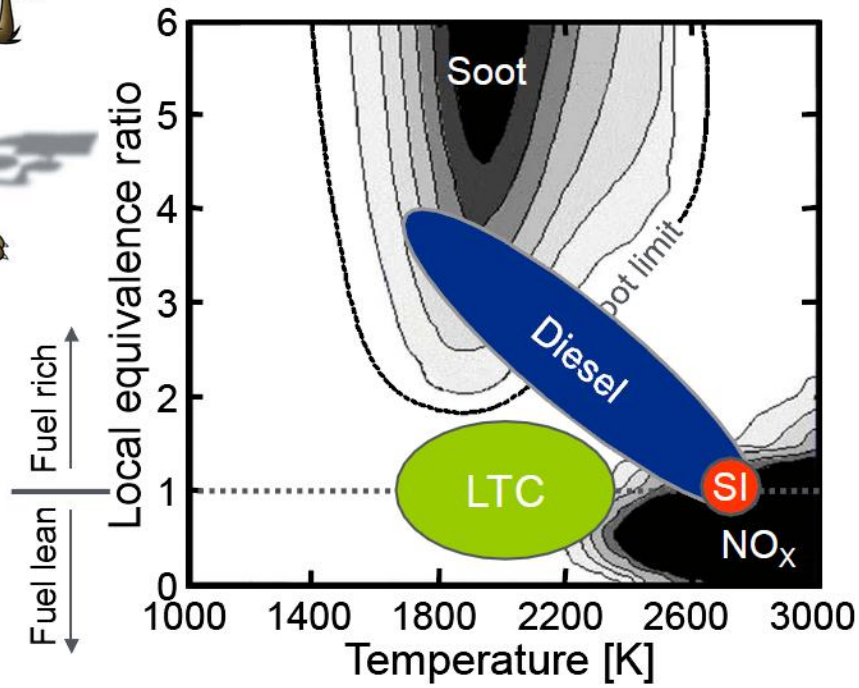
Conclusion

- Still many unknowns in detailed kinetic LTO models at almost every step of the mechanism

- LTO models are an unavoidable prerequisite in the development of cleaner engines



B. Cuenot J3P 2014



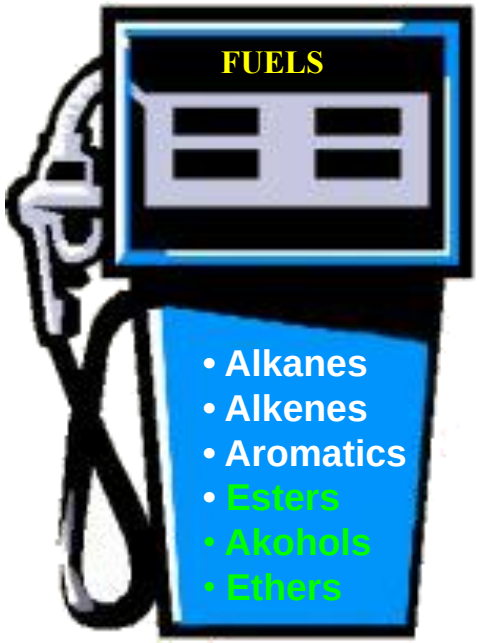
G. Singh, DOE Vehicle Technologies Office 2013

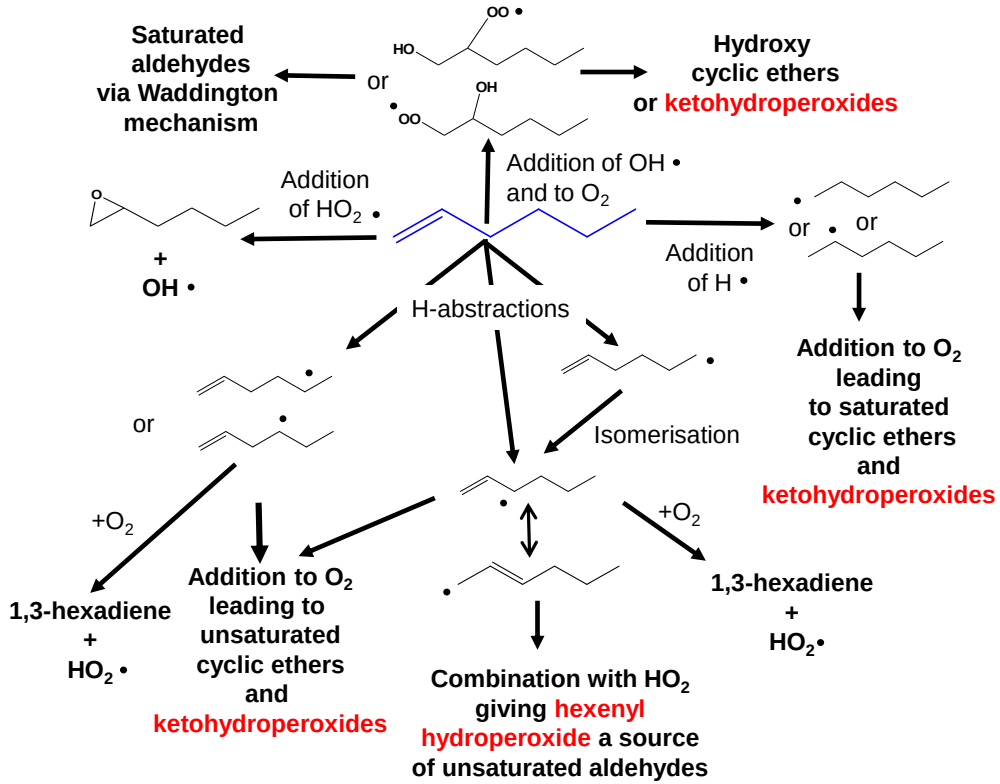
- LTO models are of even more interest with expected increasing possibilities of coupling with CFD using high performance computing

But need reliable models in extended ranges of T, P, ϕ

Conclusion

- Fuels do not only contain alkanes





F. Battin-Leclerc, O.Herbinet, F. Qi, et al. JPCA 2014

The chemistry of other fuel components (e.g. alkenes) can be still more complex

This can be worse for biofuels (see posters)

Acknowledgements

Colleagues of KinCom team

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and all the co-authors of the mentioned Nancy papers

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