SAND2022-7674C

GAS PHASE CHEMICAL PHYSICS

Chemical Kinetics

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COMBUSTION RESEARCH FACILITY
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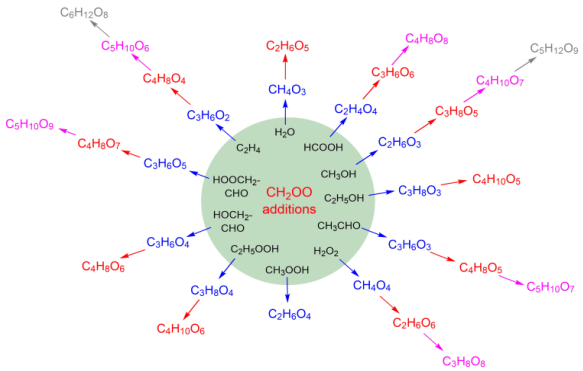
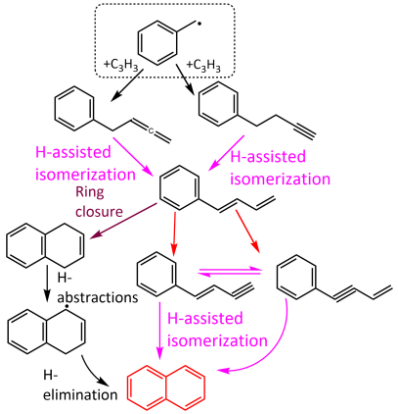
Chemical Kinetics at SNL





Non-Boltzmann Effects

Ozonolysis and Criegee Intermediate Kinetics

Low-Temperature Oxidation

ANL-SNL High-Pressure Combustion Consortium (Sheps)

Molecular Weight Growth

Theory, Automation, and Experimental Design

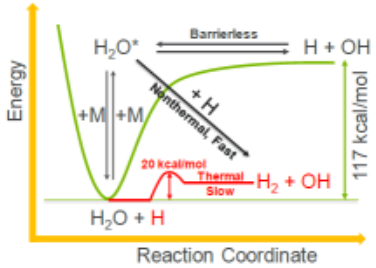
Advanced Diagnostics

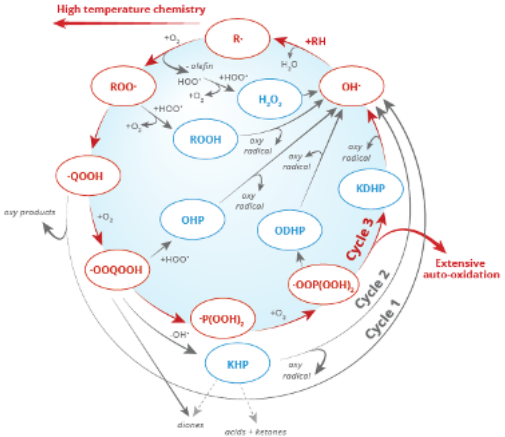
Chemical Dynamics

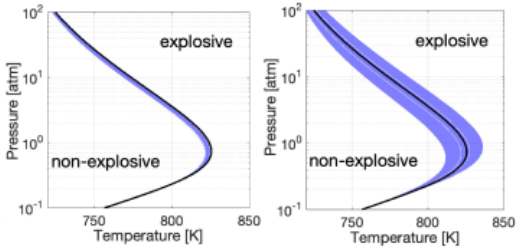
Multi-Phase Interactions

ML-Data Science (Najm/Zádor)

Exascale Catalytic Chemistry (Zádor/Najm)







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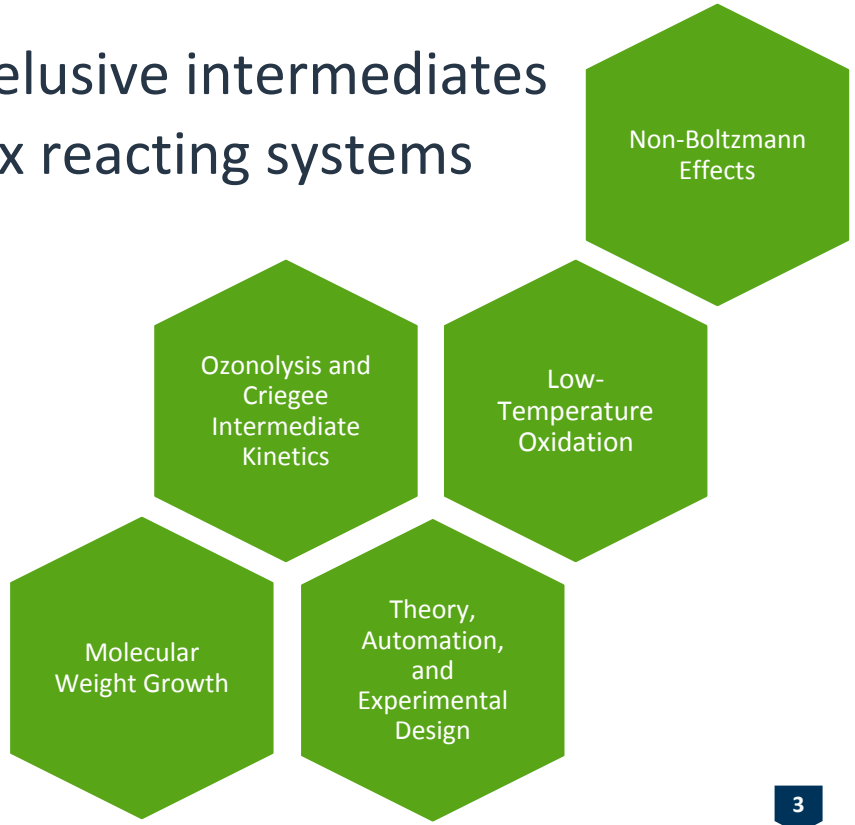
Themes in BES kinetics research at Sandia

- Direct kinetics measurements of elusive intermediates
- Multiscale interactions in complex reacting systems
- Non-equilibrium reactions
- Non-adiabatic reactions

- Low-temperature oxidation chemistry
- Molecular weight growth towards particle formation



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Chemical Kinetics at SNL:

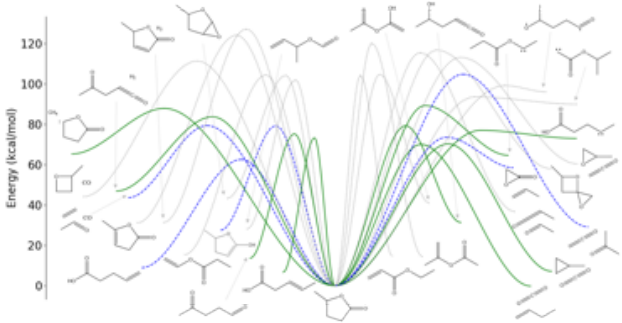
Theoretical and Computational Method Development

Molecular scale
Chemical Complexity

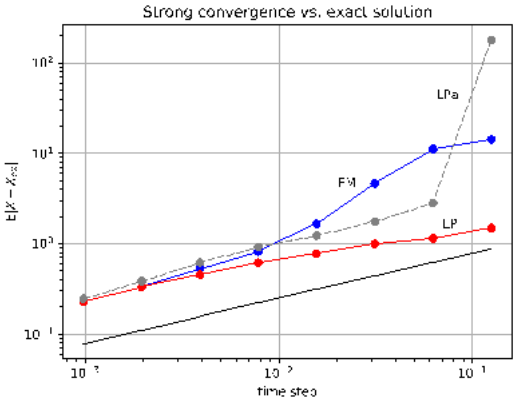
Stochastic kinetics

Non-thermal
Mesoscale Phenomena

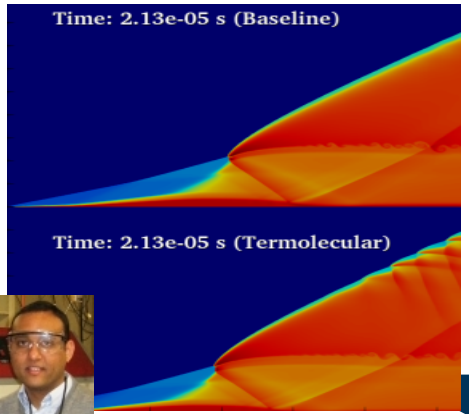
Workflow tools that automatically search for reaction pathways, compute rates & speed up discovery



Numerical methods for stochastic modeling of stiff kinetics at the mesoscale, gas phase and surface kinetics



Effects of Nonthermal H_2/O_2 Chemistry on Detonation Formation



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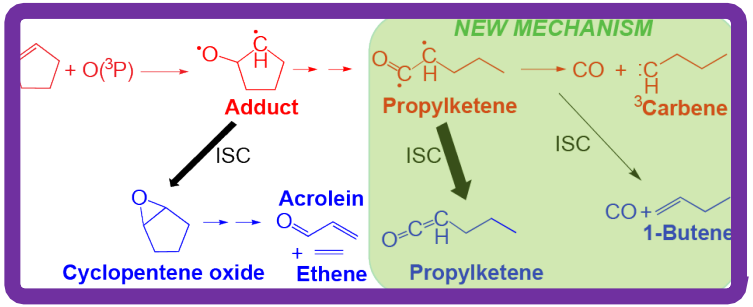
Further Developments of KinBot and Applications

- ✓ Ion fragmentation pathway exploration was demonstrated for MPIMS data interpretation
- ✓ Stereochemistry-aware PES search
- ✓ Search on triplet and singlet PES are both successful
- ✓ Workflow is enabled to run on NERSC via Fireworks and Q-Chem integration (within ML project)

Cyclopentene + O^3P

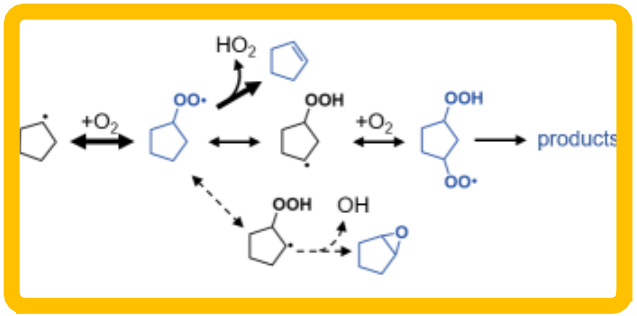
ISC beyond the entrance channel



Ramasesha *et al., J. Phys. Chem. A.*, **2021,** 125, 9785-9801

Low-temperature cyclopentane oxidation

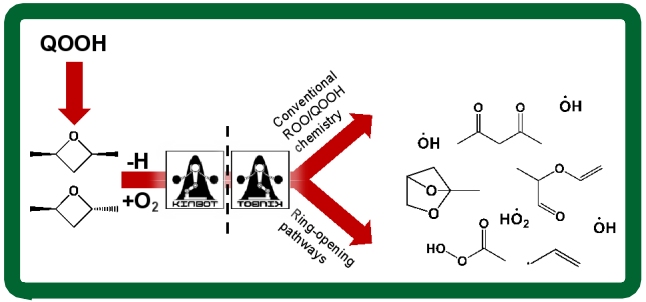
Mechanism and kinetics w/ L. Sheps and HPCC



Sheps *et al., J. Phys. Chem. A,* **2021,** 125, 4467-4479

Oxidation chemistry of DMO

Strongly stereoisomer-dependent kinetics w/ B. Rotavera (UGA)



Doner *et al., Faraday Discuss.,* **2022,** in press

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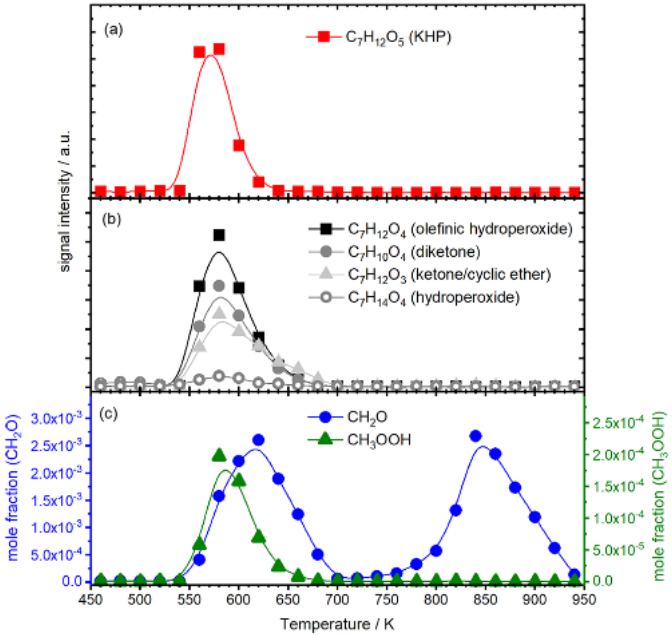
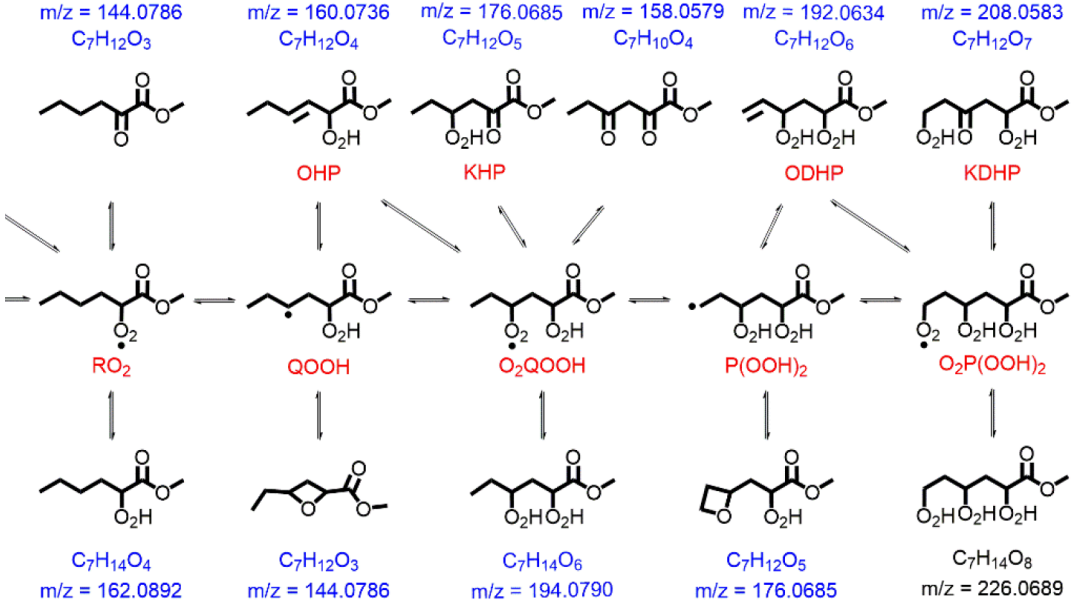
Low-Temperature Oxidation of Methyl Hexanoate





GAS PHASE CHEMICAL PHYSICS

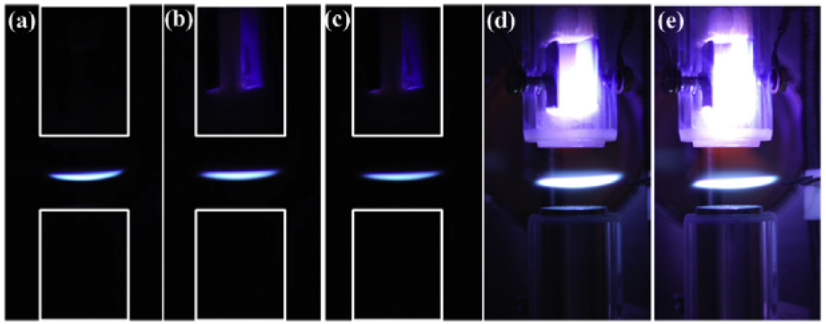
A. Rousso *et al., J. Phys. Chem. A,* **2020,** 124, 9897-9914
Invited Feature Article, ACS Editors' Choice, Open Access

Ozone Interactions with Hydrocarbons:
Ignition and Atmospheric Chemistry

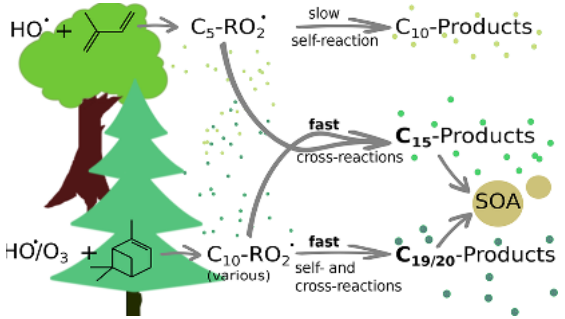
- Reactions of ozone with C=C double bonds

Ozonolysis mechanism laid out by Rudolf Criegee

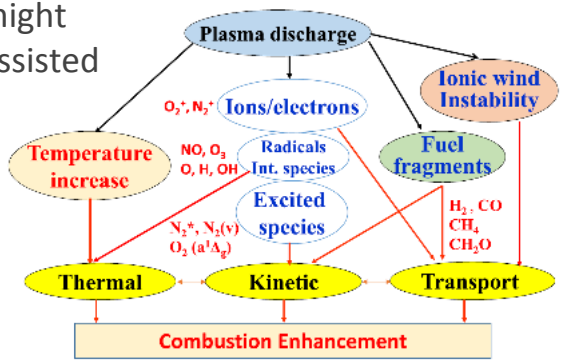
R. Criegee, *Angew. Chem. Int. Ed. Engl.* (1975)



- Ozonolysis reactions are important in the atmosphere:



- Ozone-fuel interactions might be important in plasma-assisted combustion:
  - Fuel-ozone interactions?
  - Thermal dissociation?
  - Enhancement effects on LTC chemistry?

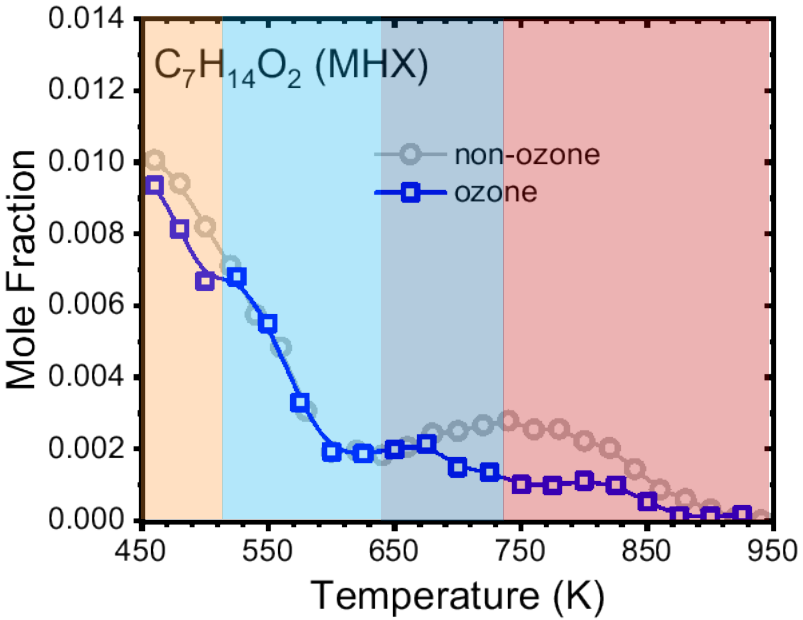


GAS PHASE CHEMICAL PHYSICS

Y. Ju, *Proc. Combust. Inst.*, **2021,** 38, 83-119

T. Berndt *et al., Environ. Sci. Technol.*, **2018,** 52, 11069-11077

Low-Temperature Oxidation of Methyl Hexanoate – Ozone Addition



- significantly more fuel consumption in the intermediate temperature range
- very little NTC behavior when ozone added
- almost no change in LTC fuel profile
- small increase in fuel consumption

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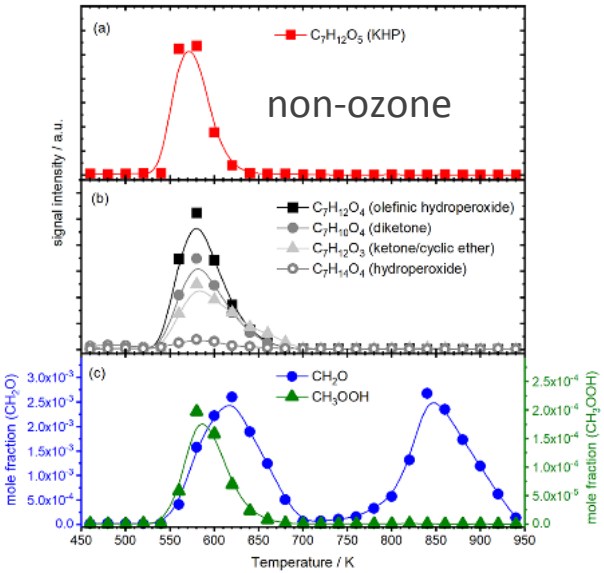
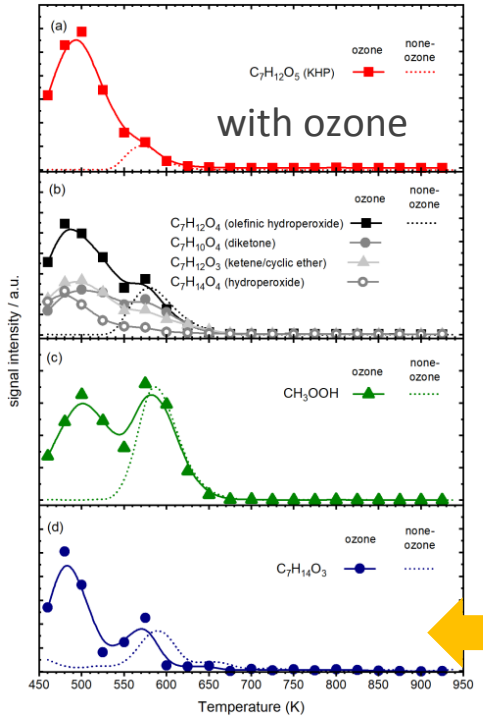
A. Rousso *et al., J. Phys. Chem. A,* **2020,** 124, 9897-9914
Invited Feature Article, ACS Editors' Choice, Open Access

Extreme Low-Temperature Combustion (ELTC):
Ozone-Initiated Oxidation of Methyl Hexanoate





At temperatures below standard LTC chemistry:

- ✓ concentrations are of similar order or much higher concentrations than LTC
- ✓ smaller intermediates are observed but at *lower* concentrations than LTC regime
  - ➢ no subsequent breakdown
  - ➢ quasi-stable hydroperoxide species formation

$$2\ RO_2 \rightleftarrows R'O + ROH + O_2$$

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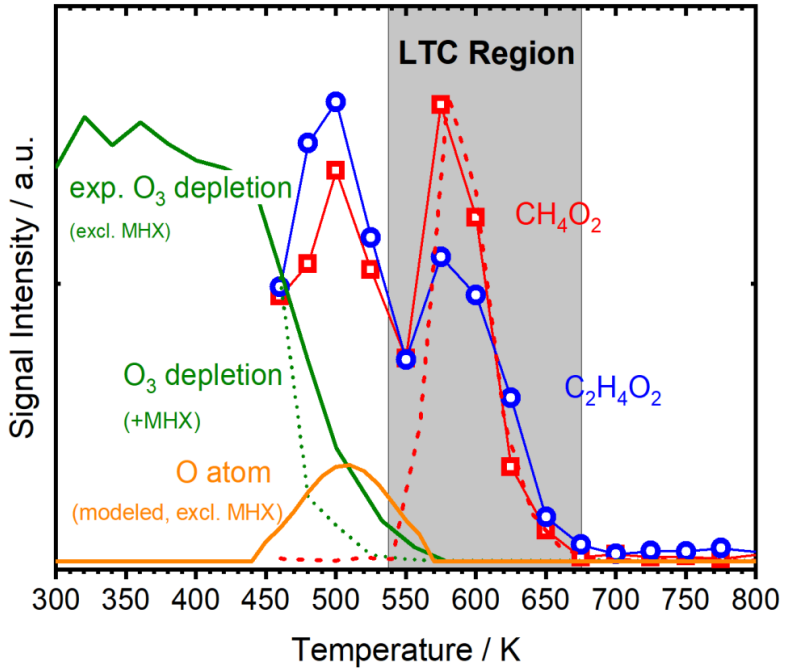

- ✓ modeled ozone decomposition without MHX
- ✓ peak atomic O production overlaps with experimental peaks in ELTC regime
- ✓ lines up with accelerated O_3 depletion due to fuel addition
- ✓ O radical chemistry is driving force for hydroperoxide chemistry – *no ozonolysis likely at play*
- ✓ in LTC regime, traditional LTC pathways accelerate – similar order/faster than ozone decomposition
  - ✓ O atom makes slight changes but does not drastically alter pathways

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A. Rousso *et al., J. Phys. Chem. A,* **2020,** 124, 9897-9914
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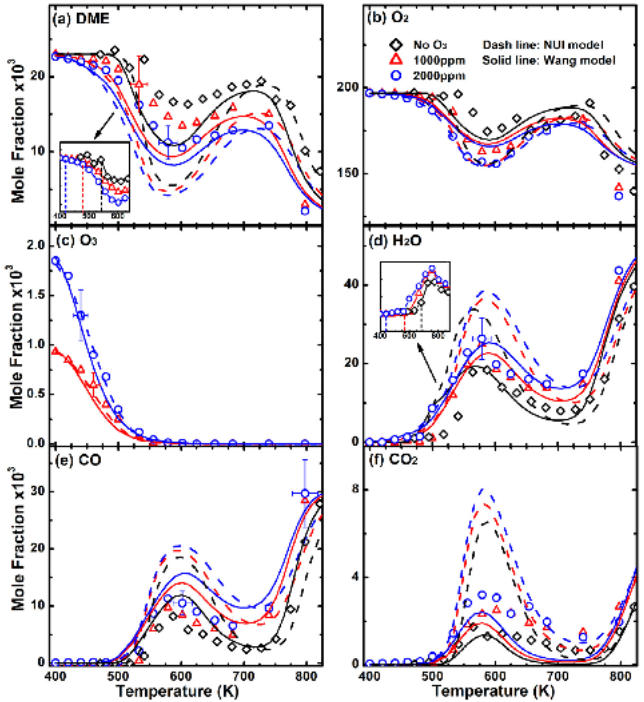
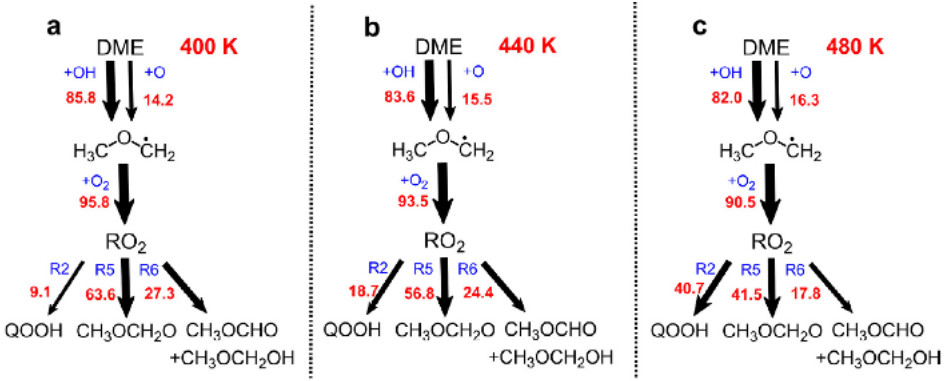
Low-Temperature Oxidation of DME

Quantification of the Main Species



$$CH_3OCH_2 + O_2 \rightleftarrows CH_3OCH_2O_2 \quad (R1)$$
$$CH_3OCH_2O_2 \rightleftarrows CH_2OCH_2O_2H \quad (R2)$$
$$CH_2OCH_2O_2H + O_2 \rightleftarrows O_2CH_2OCH_2O_2H \quad (R3)$$
$$O_2CH_2OCH_2O_2H \rightleftarrows HOOCH_2OCHO + OH \quad (R4)$$
$$2\ CH_3OCH_2O_2 \rightleftarrows 2\ CH_3OCH_2O + O_2 \quad (R5)$$
$$2\ CH_3OCH_2O_2 \rightleftarrows CH_3OCHO + CH_3OCH_2OH + O_2 \quad (R6)$$



K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

H. Liao *et al., Combust. Flame,* **2020,** 214, 277-286

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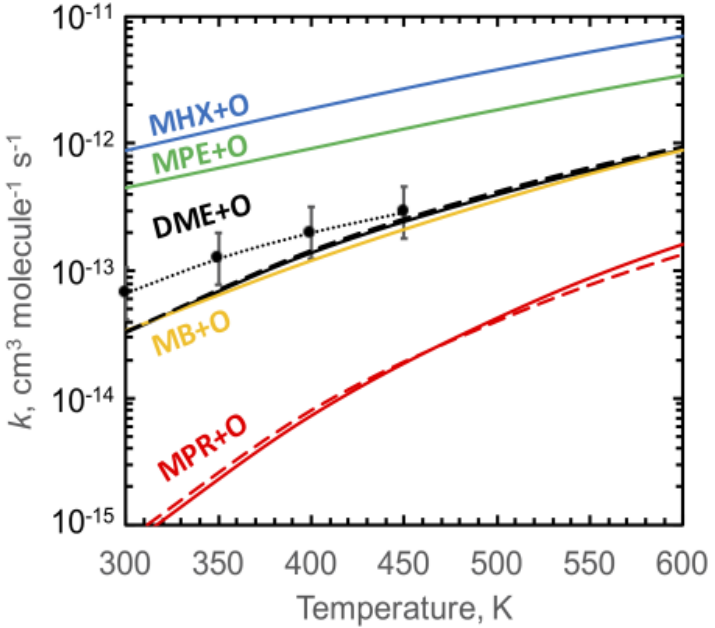
Extreme Low-Temperature Combustion (ELTC):
Ozone-Initiated Oxidation of Methyl Hexanoate

Why do we see increased reactivity at around 450K when this was not observed for species such as DME?



Theoretical calculations indicate:

- Atomic O initiated H-abstraction seems to be more sensitive to fuel structure than conventional O_2 abstraction
- Rate constant for O + MHX more than an order of magnitude faster than O + DME

A. W. Jasper, Argonne

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Extreme Low-Temperature Combustion (ELTC):
Ozone-Initiated Oxidation of Methyl Hexanoate

$O_3 \rightleftarrows O_2 + O(^3P)$
$RH + O \rightleftarrows R + OH$
$R + O_2 \rightleftarrows RO_2 \rightleftarrows QOOH \rightleftarrows$

$O + O\ (+M) \rightleftarrows O_2\ (+M)$

$OH + O_3 \rightleftarrows HO_2 + O_2$
$HO_2 + O_3 \rightleftarrows OH + 2\ O_2$
net: $OH + 2\ O_3 \rightleftarrows OH + 3\ O_2$

$2\ RO_2 \rightleftarrows 2\ RO + O_2$
$2\ RO_2 \rightleftarrows R'O + ROH + O_2$

- ✓ ozone decomposition is slow, but faster than peroxide chemistry (extremely slow)
- ✓ boosted reactivity compared to non-ozone case, but not enough to continue fuel breakdown
- ✓ may be sensitive to fuel structure
- ✓ likely see the formation of several different isomers to traditional LTC regime

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A. Rousso *et al., J. Phys. Chem. A,* **2020,** 124, 9897-9914
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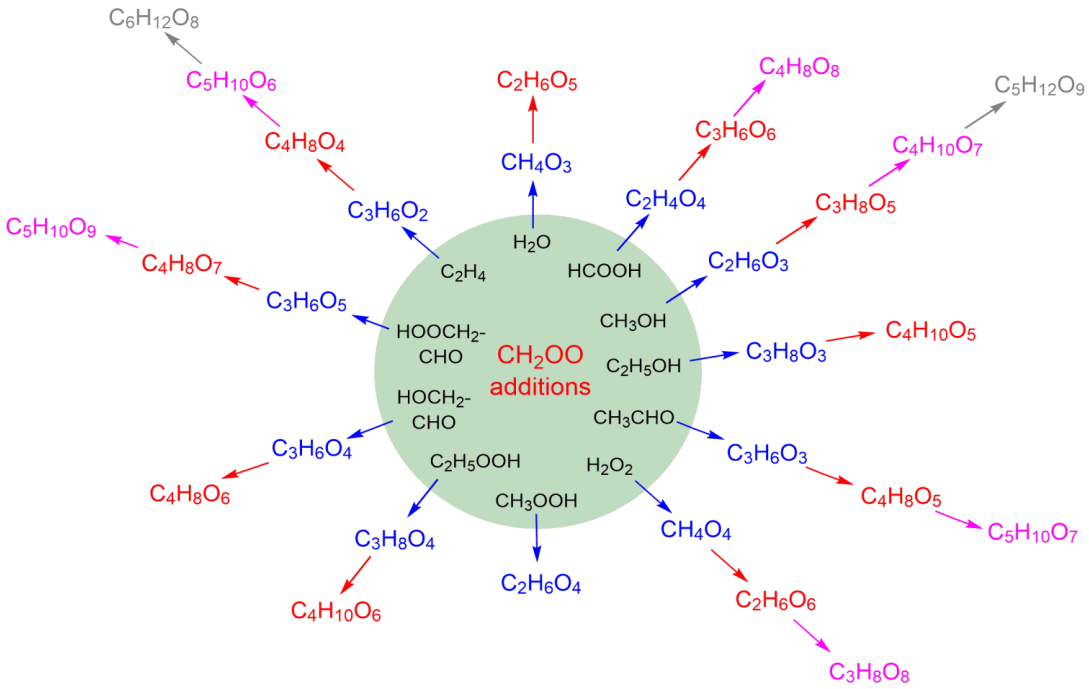
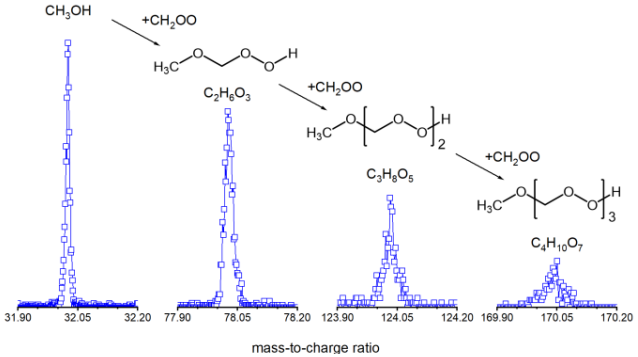
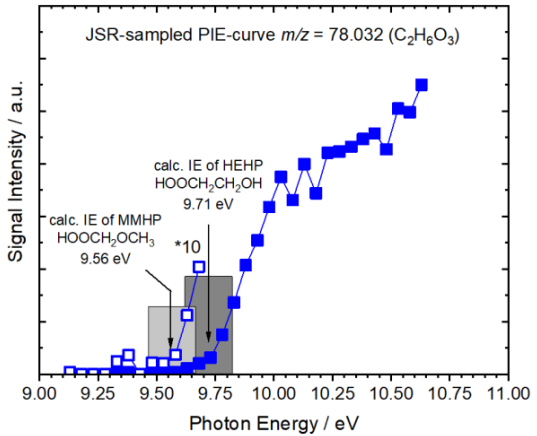
Ozone Interactions with C=C Double Bonds

Criegee Intermediate Reactions







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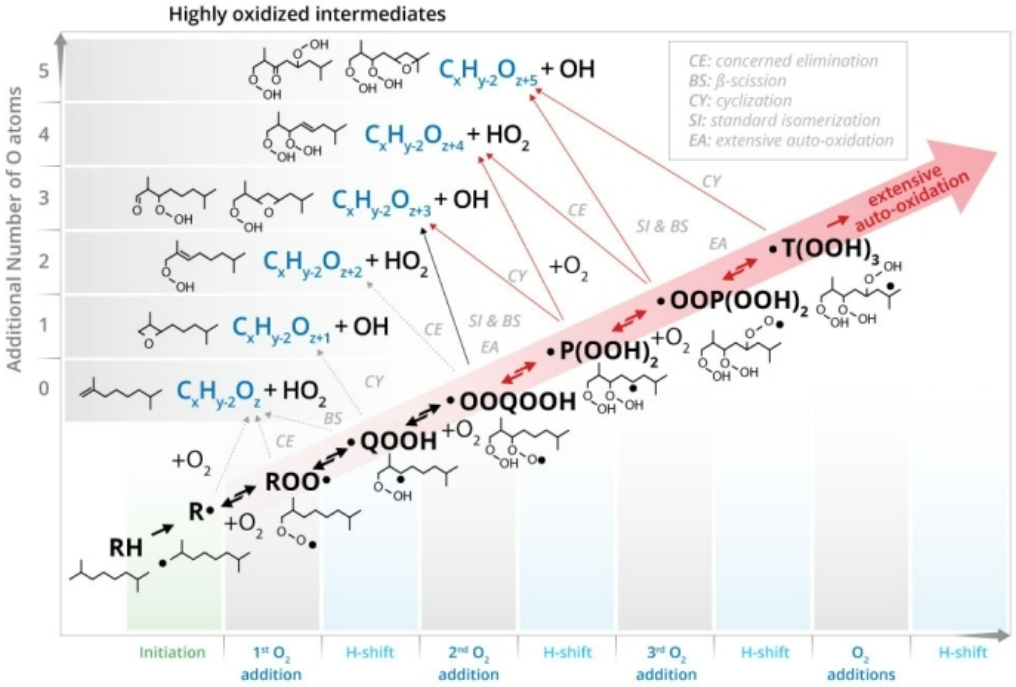
A. C. Rousso, A. W. Jasper, Y. Ju, N. Hansen, *J. Phys. Chem. A,* **2018,** 122(43), 8674-8685 and *Phys. Chem. Chem. Phys.,* **2019,** 21, 7341-7357

Highly Oxygenated Molecules (HOM):
From Gas-Phase Oxidation to Atmospheric Aerosol



Z. Wang *et al., Proc. Nat. Acad. Sci.,* **2017,** 114(50), 13102-13107

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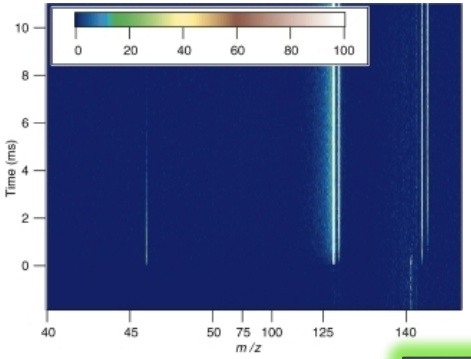
Ozone-initiated molecular weight growth

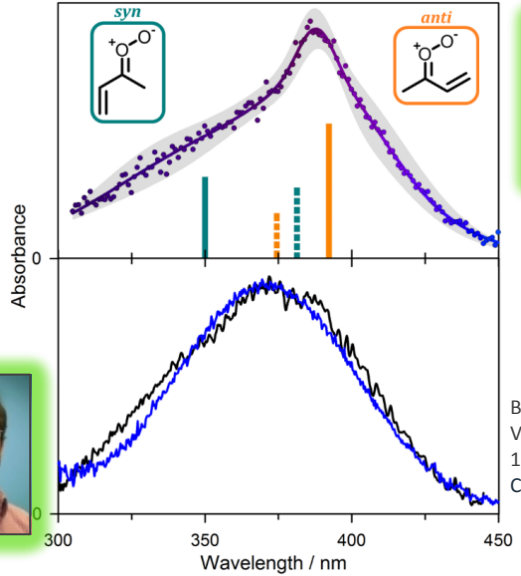
"Oligomerization" reactions of carbonyl oxides and formation of highly oxygenated compounds, as seen in JSR, may form atmospheric aerosol

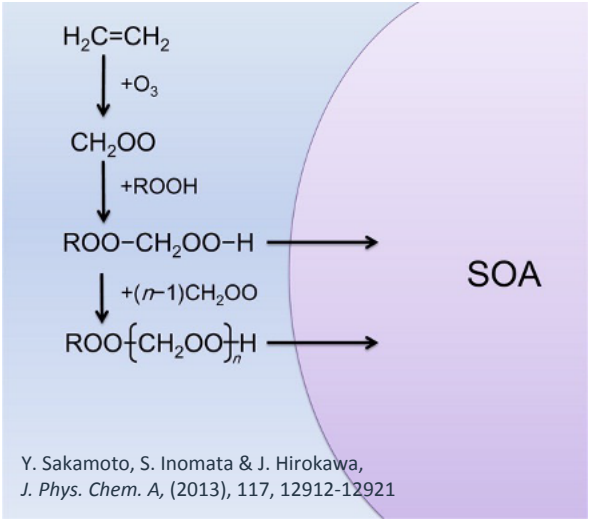
Proposed mechanism is insertion

We can study elementary Criegee reactions

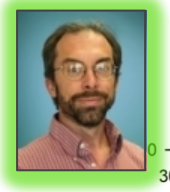


Welz et al., *Science* **335**, 204 – 207 (2012);
CAT et al. *Science* **340**, 177–180 (2013)





Y. Sakamoto, S. Inomata & J. Hirokawa,
J. Phys. Chem. A, (2013), 117, 12912-12921



Barber, Klippenstein, Lester et al., *J. Am. Chem. Soc.* 2018, 140, 34, 10866–10880
Vansco , Klippenstein, Lester et al., *J. Am. Chem. Soc.* 2019, 141, 38, 15058–15069
Caravan, Sheps, Lester, Klippenstein, CAT et al., *PNAS* 117, 9733-9740 (2020)

GAS PHASE CHEMICAL PHYSICS

Sequence built from initial reaction with acid

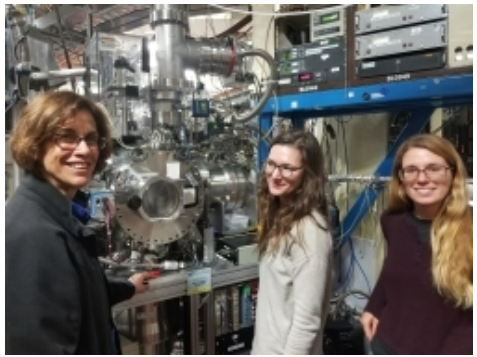
Fast ("supercollisional") reaction general for CH_2OO with all organic acids

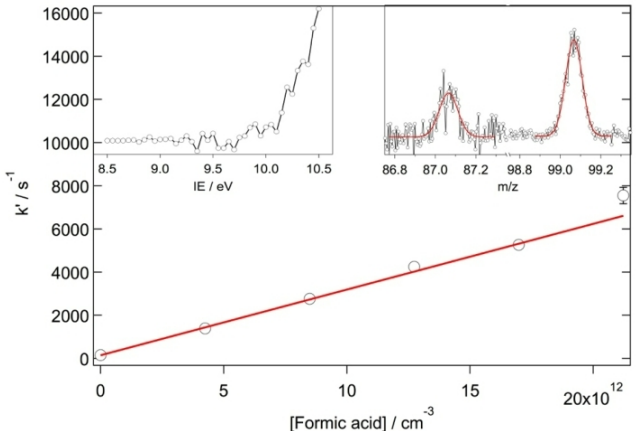
(Welz et al., *Angew. Chem. Int. Ed.* **53**, 4547-4550 (2014); Chhantyal-Pun et al., *ACS Earth Space Chem.* 2, 833–842 (2018); CAT et al, *Environ. Sci. Technol.* **53**, 1245-1251 (2019))

Isoprene-derived conjugated Criegee intermediates also react rapidly

(Caravan et al., *Proc. Nat. Acad. Sci. USA* 117, 9733-9740 (2020); Vansco et al., *Phys. Chem. Chem. Phys.*, 2020, 22, 26796-26805; Vansco et al., *Molecules* 26, 3058 (2021))

Reaction with acid forms a hydroperoxide product

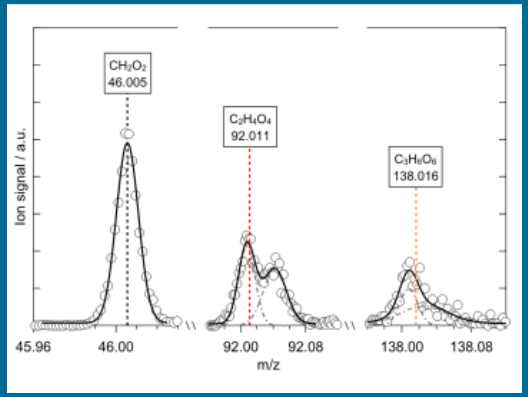


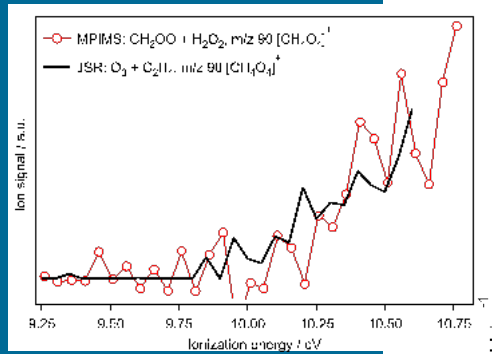


Caravan, Sheps, Lester, Klippenstein, CAT et al., *PNAS* 117, 9733-9740 (2020)

GAS PHASE CHEMICAL PHYSICS

Sequence started by CH_2OO reaction with formic acid – identified in JSR



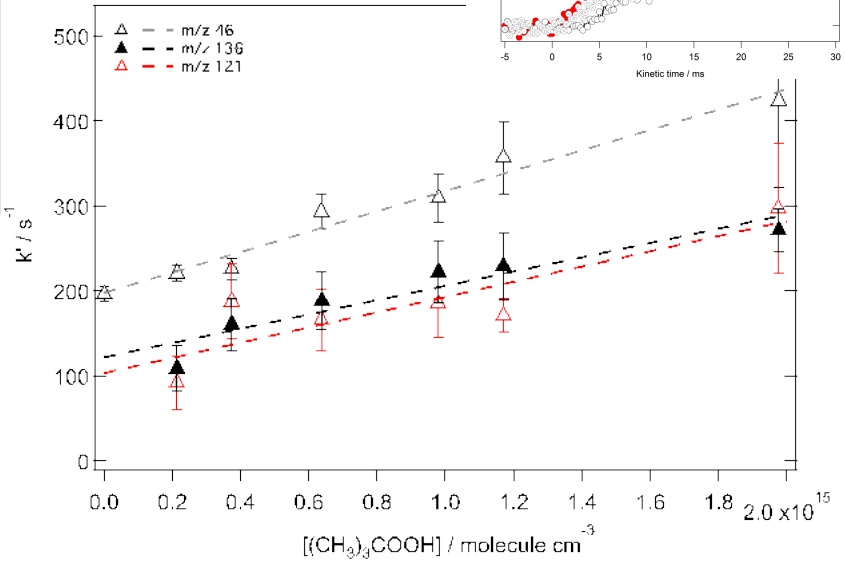


Rousso, Jasper, Ju, Hansen, Phys. Chem. Chem. Phys., 2019, 21, 7341-7357

Product photoionization spectra from ozonolysis can be compared to photolytic "direct" kinetics – known to be hydroperoxymethyl formate

Cabezas and Endo, ***Phys. Chem. Chem. Phys.***, 2019, **21**, 18059-18064

Can measure representative insertion reactions of hydroperoxides



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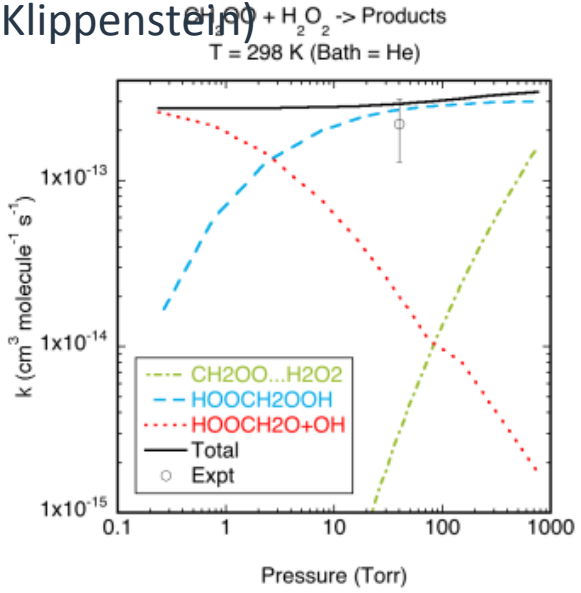
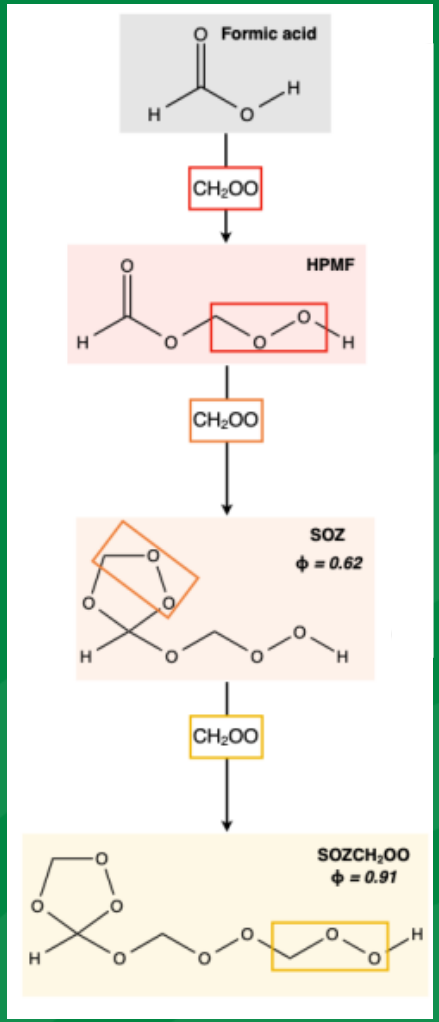
Compare measured representative reactions to theory (Klippenstein)



Theory can provide reliable values for unmeasured rate coefficients



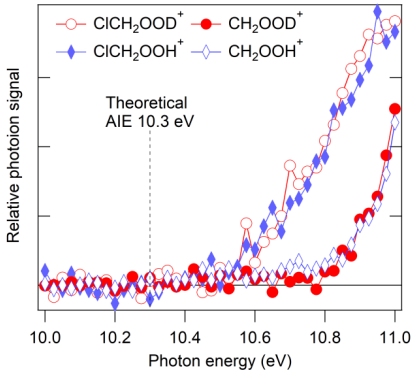
Confirms and quantifies previous proposals inferred from laboratory ozonolysis measurements

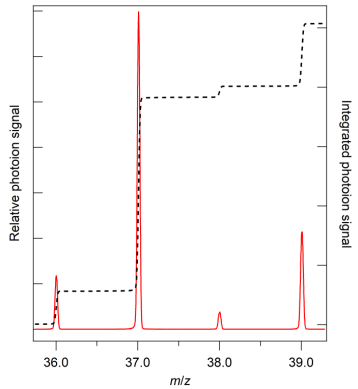
Some unexpected results – stabilized hydroperoxy-SOZ product

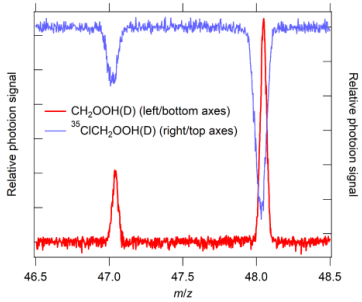
Continue to work on theory-experiment comparisons

GAS PHASE CHEMICAL PHYSICS

1,2-insertion reactions of Criegee intermediates

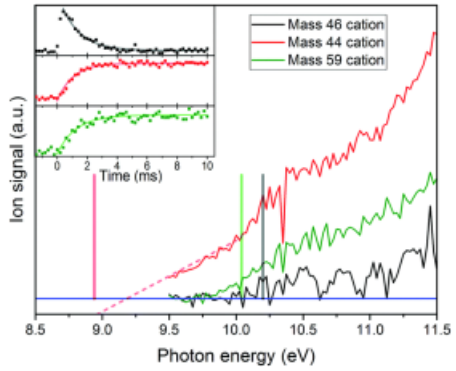


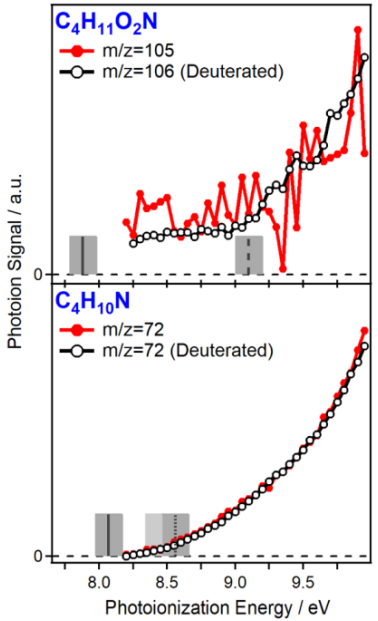




Chloro(hydroperoxy)methane formation from reaction of CH_2OO with HCl and DCl
CAT et al., *Mol. Phys.* **119**, e1975199, (2021)

Chhantyal-Pun et al, *Phys. Chem. Chem. Phys.* **21,** 14042-14052 (2019)





Conformer dependence of insertion reaction of CH_3CHOO Criegee intermediate with dimethylamine

Vansco et al., *J. Phys. Chem. A* **126**, 710–719 (2022).

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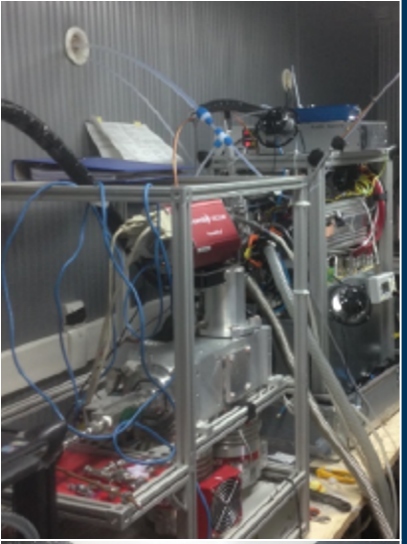
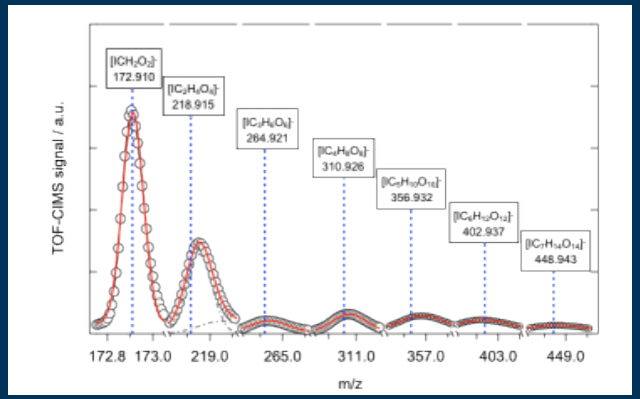
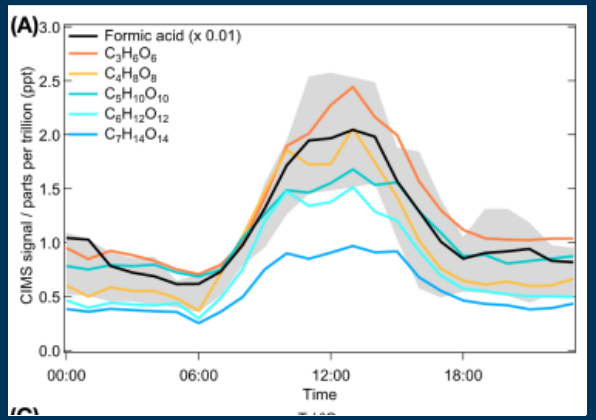


These sequences also appear to be linked to aerosol in the Amazon rainforest

CIMS measurements of aerosol and gas phase in Brazil



Sequences of CH_2OO addition



Diurnal profiles suggest a common origin

Caravan, Ju, Hansen, Percival, Klippenstein et al., in preparation

← Carl Percival, Tom Bannan et al.

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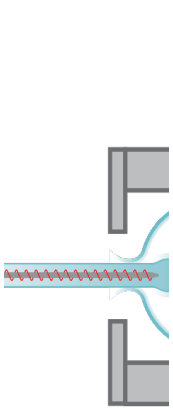
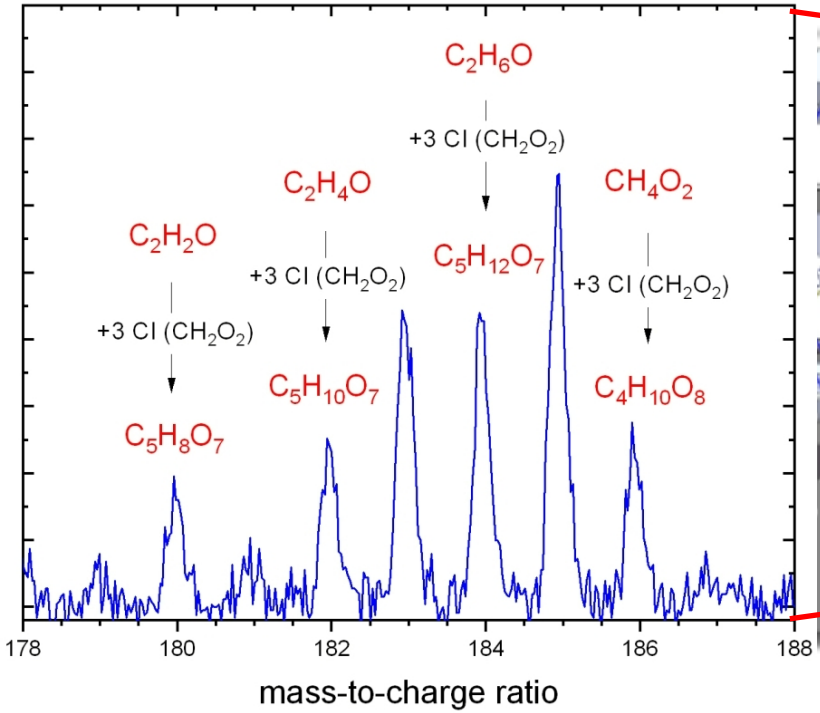
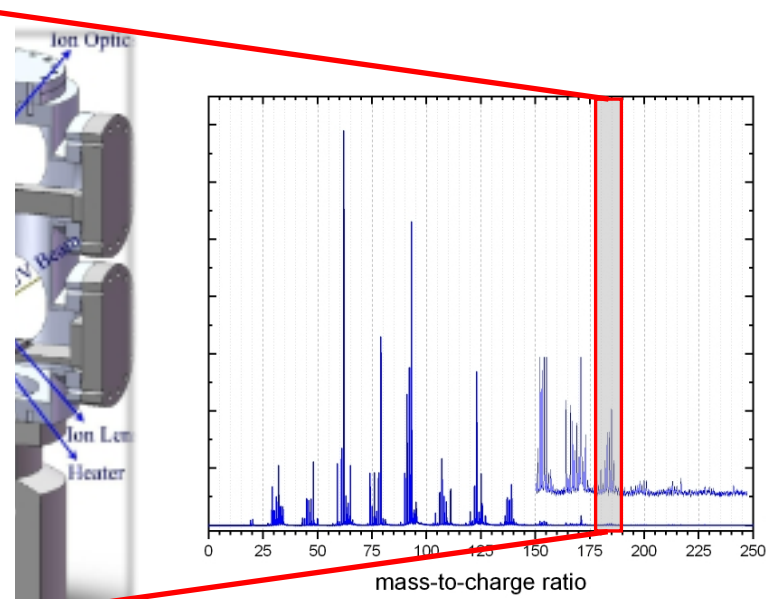
Chemical Composition of Particles after Ozonolysis

in collaboration with K. R. Wilson and M. Zeng (LBNL)



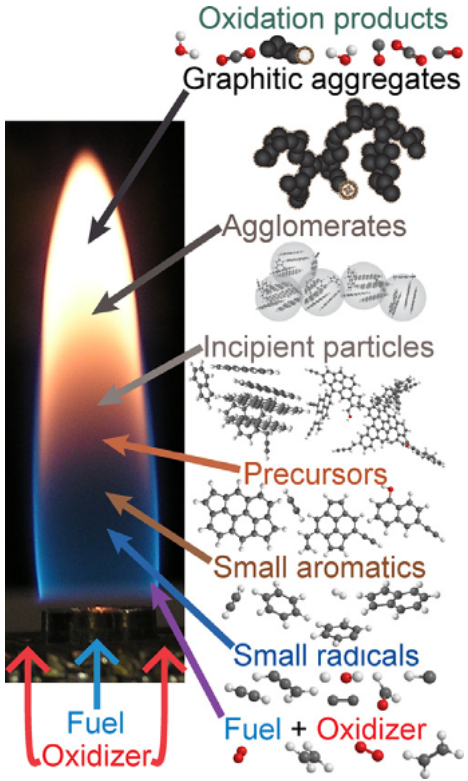




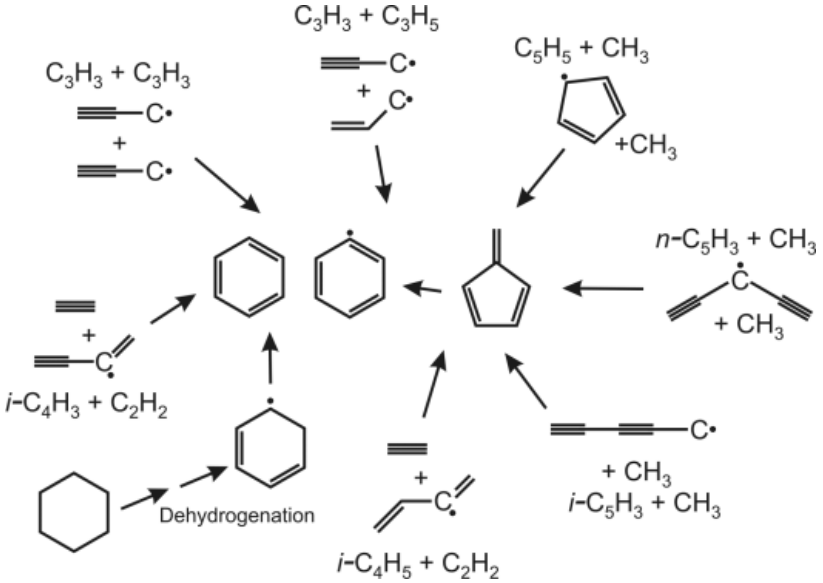
GAS PHASE CHEMICAL PHYSICS

N. Hansen, M. Zeng, K. R. Wilson, manuscript in preparation

Molecular-Weight Growth in Extreme Environments

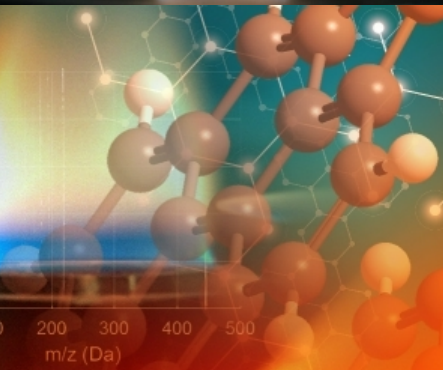


H. A. Michelsen, *Proc. Combust. Inst.*, **2017,** 36(1), 717-735



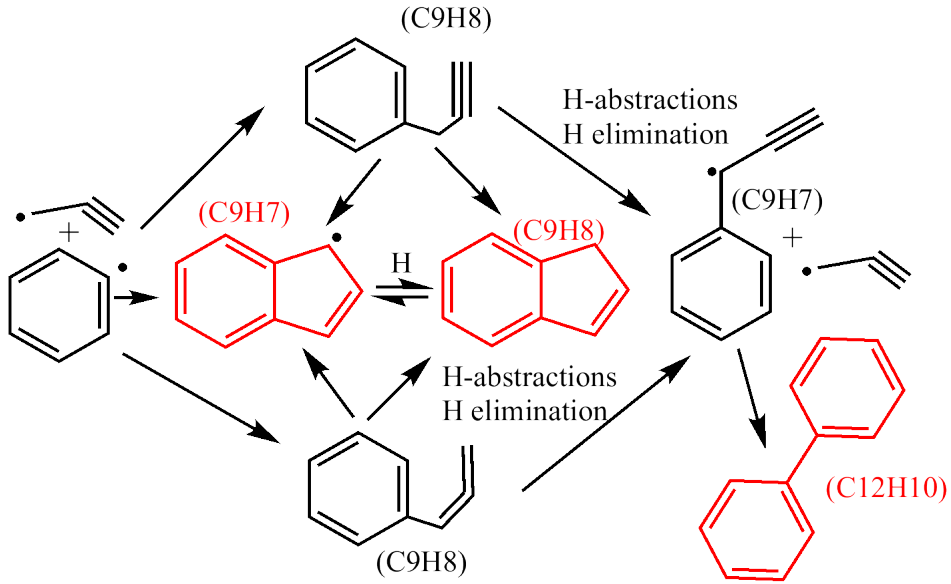
- ✓ many different reactions can contribute towards benzene formation
- ✓ they all involve resonantly stabilized radicals
- ✓ the importance of these reactions depends on the fuel consumption pathways
- ✓ fulvene is an important intermediate

N. Hansen *et al., Combust. Expl. Shock Waves,* **2012,** 48, 508-515

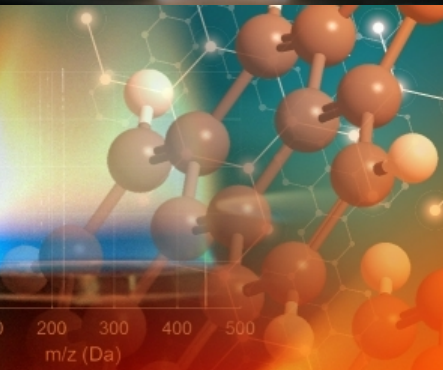


Molecular-Weight Growth:

C_3H_3 Addition Mechanism – Indene Formation

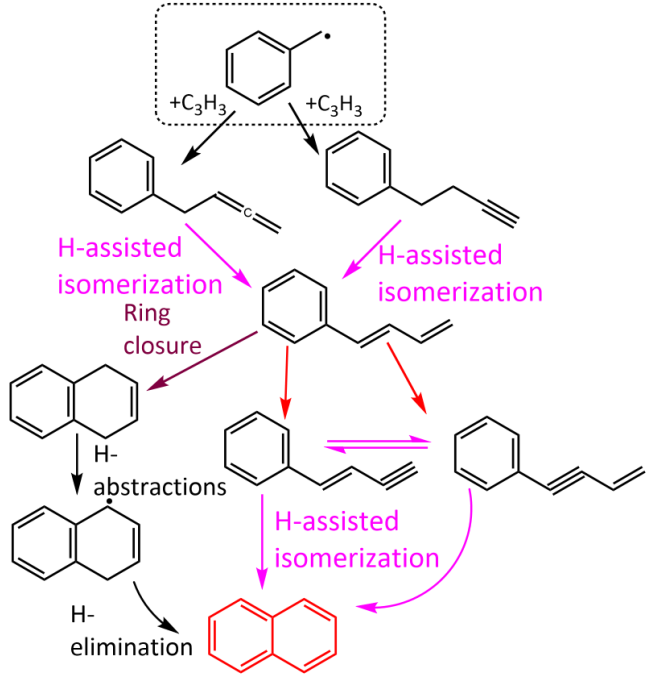


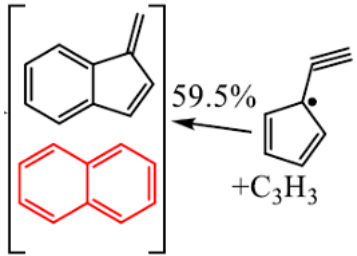
G. Kukkadapu, S. W. Wagnon, W. J. Pitz, N. Hansen, *Proc. Combust. Inst.*, **2021,** 38(1), 1477-1485



Molecular-Weight Growth:

C_3H_3 Addition Mechanism – Naphthalene Formation

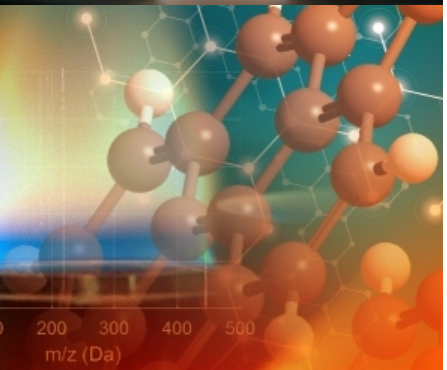




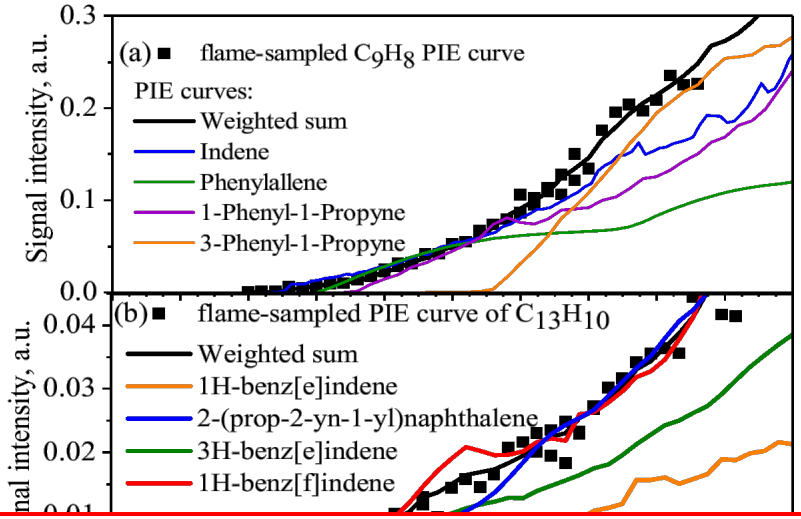
Summary:

- ✓ C_3H_3 is an important intermediate to make 5- and 6-memberd ring structures beyond benzene
- ✓ aliphatically substituted aromatics are important intermediates
- ✓ C_7H_5 is an important intermediate

G. Kukkadapu, S. W. Wagnon, W. J. Pitz, N. Hansen, *Proc. Combust. Inst.,* **2021,** 38(1), 1477-1485
N. Hansen, B. Yang, M. Braun-Unkhoff, A. Ramirez, G. Kukkadapu, *Combust. Flame,* **2022,** in press

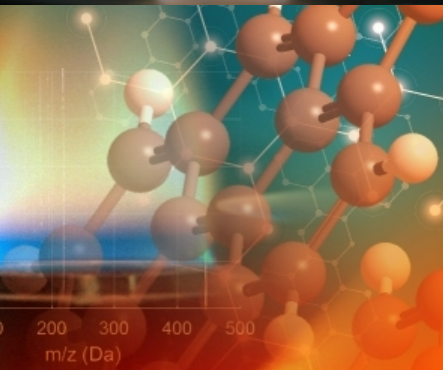


Molecular-Weight Growth:
Limitations of Photoionization Efficiency (PIE) Curves

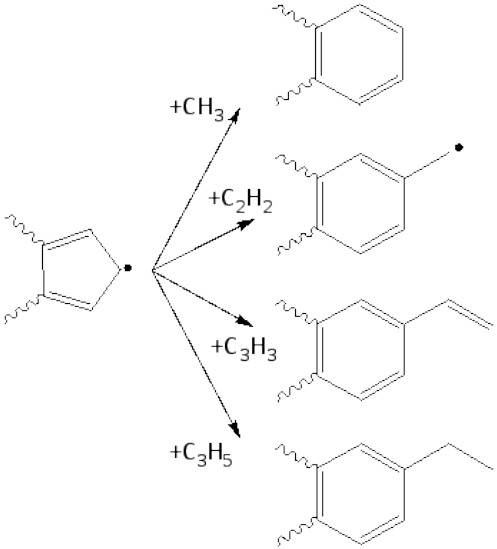


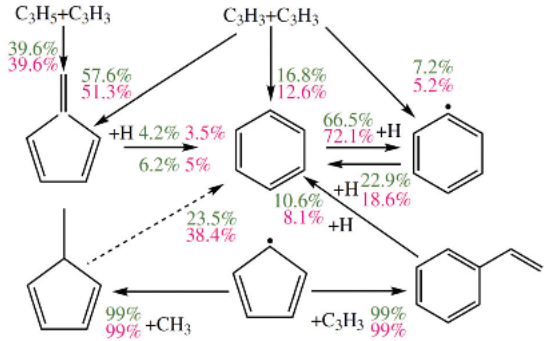
- Smaller differences in heats of formation and similar structural features result in almost identical IE's and indistinguishable PIE curves for larger species
- IE's and PIE curves may not be known and need to be measured/calculated

G. Kukkadapu, S. W. Wagnon, W. J. Pitz, N. Hansen, *Proc. Combust. Inst.*, **2021,** 38(1), 1477-1485



Molecular-Weight Growth:
Ring-Enlargement Reactions

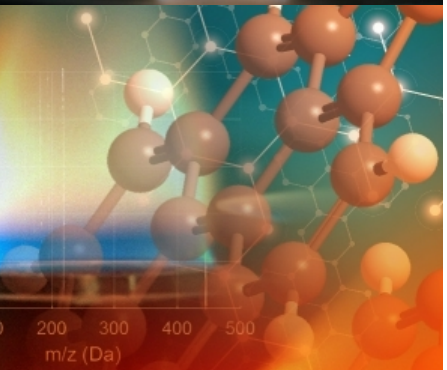




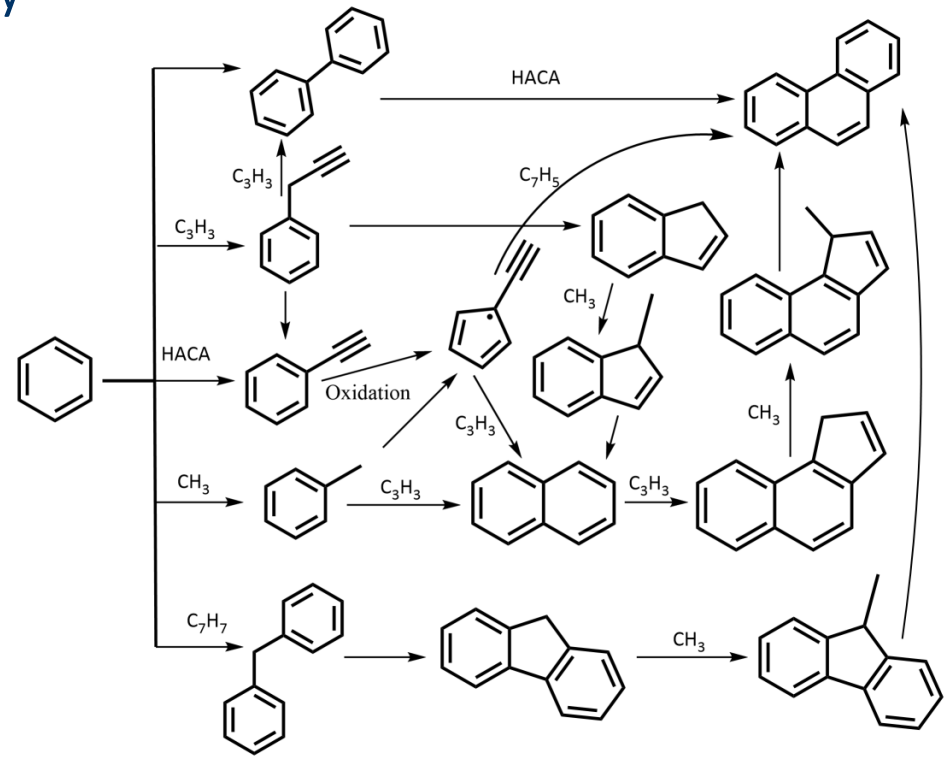
M. Baroncelli, Q. Mao, S. Galle, N. Hansen, and H. Pitsch, *Phys. Chem. Chem. Phys.*, **2020,** 22, 4699-4714

M. Baroncelli, Q. Mao, N. Hansen, H. Pitsch, *Combust. Flame,* **2021,** 230, 111427

R. I. Kaiser and N. Hansen, *J. Phys. Chem. A,* **2021,** 125, 3826−3840

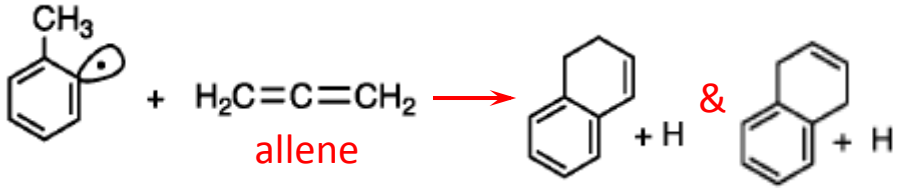


Molecular-Weight Growth:
Summary

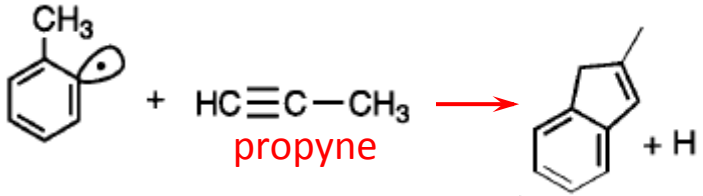


R. I. Kaiser and N. Hansen, *J. Phys. Chem. A,* **2021,** 125, 3826−3840
N. Hansen, B. Yang, M. Braun-Unkhoff, A. Ramirez, G. Kukkadapu, *Combust. Flame,* **2022,** in press

Isomeric C_3H_4 Controls Five- vs. Six-Member PAH Ring Formation

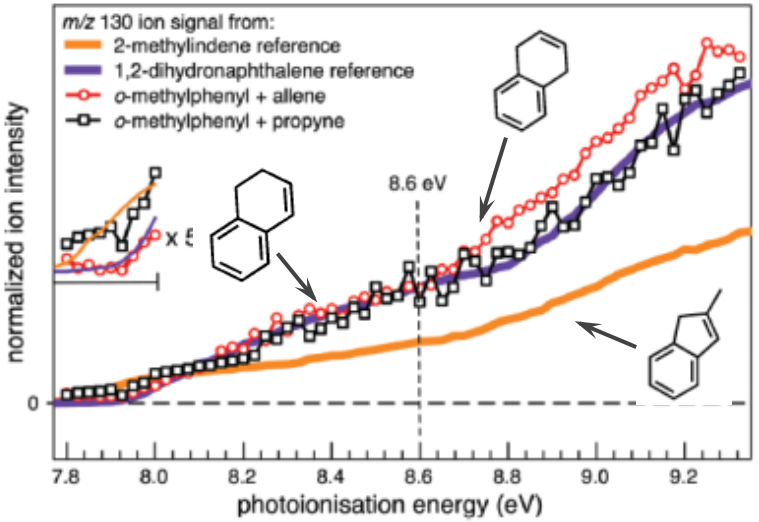


ortho-methylphenyl



New Insights

- ortho CH_3 group required for 2nd ring formation
- Isomeric nature of C_3H_4 reactant determines whether (6,6) or (6,5) ring PAHs are formed.
- 5-member rings induce non-planarity in PAHs.



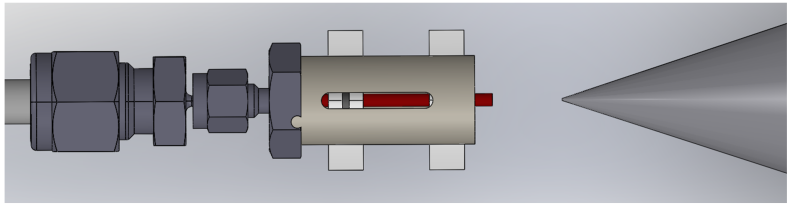
Five *vs.* six membered-ring PAH products from reaction of *o*-methylphenyl radical and two C_3H_4 isomers†

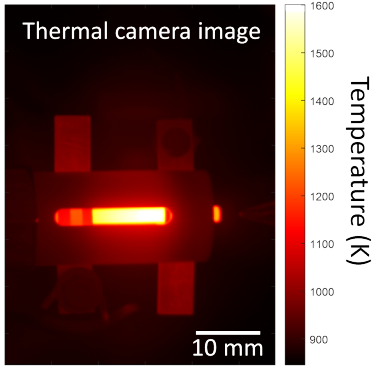
Oisin J. Shiels, ‡[a] Matthew B. Prendergast, ‡§[a] John D. Savee,[b] David L. Osborn,[b] Craig A. Taatjes,[b] Stephen J. Blanksby,[c] Gabriel da Silva[d] and Adam J. Trevitt*[a]

Cite this: *Phys. Chem. Chem. Phys.*, 2021, **23**, 14913

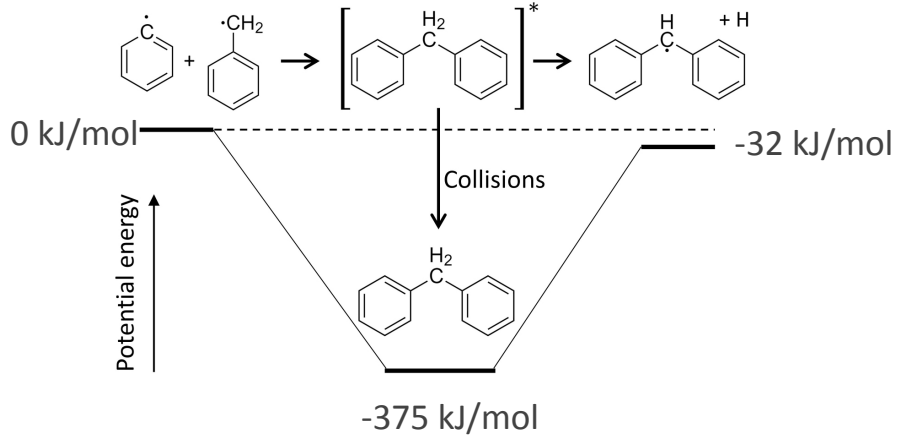
Molecular-Weight Growth via Radical-Radical Reactions

Importance of Well-Skipping Reactions





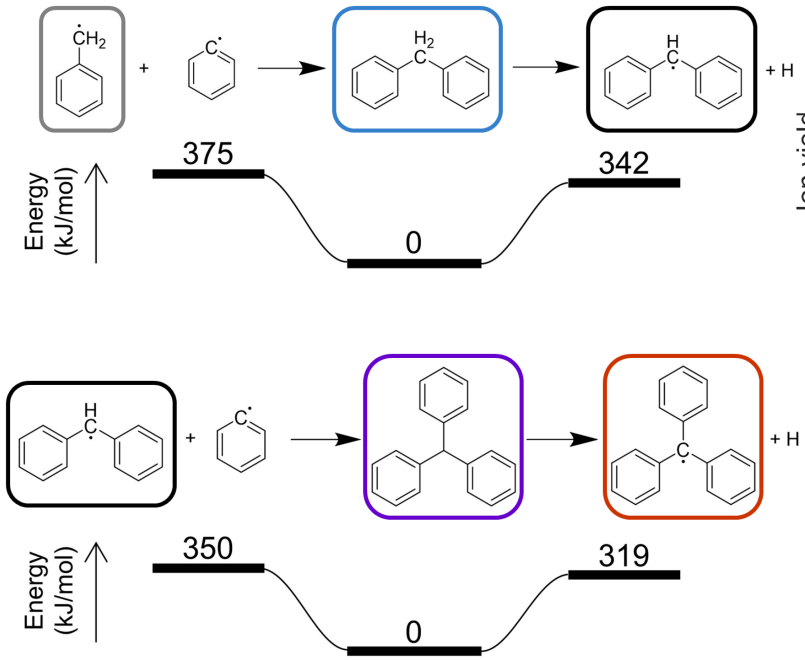
$$Radical + Radical \rightarrow [Adduct]^* \rightarrow Radical + Radical$$

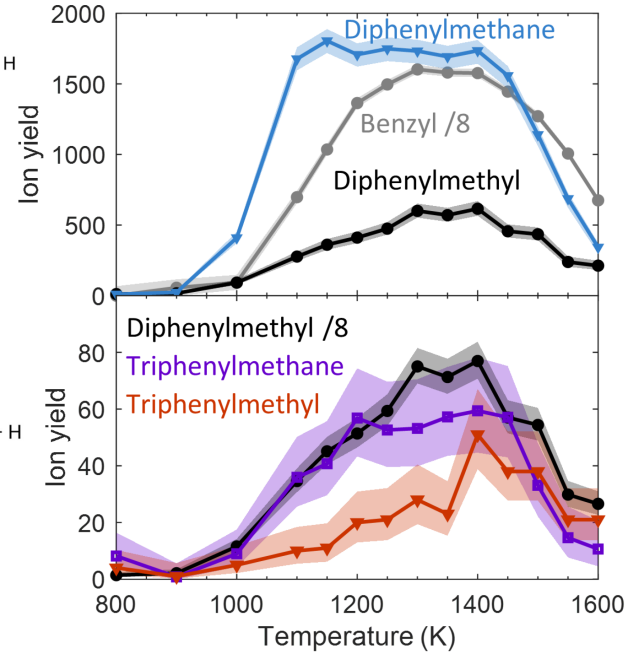


Radical-propagating
Reactivation only required when caught in the “well”
Rate depends on temperature and pressure

D. E. Couch, A. J. Zhang, C. A. Taatjes, and N. Hansen,
Angew. Chem. Int. Ed., **2021,** 60, 27230-27235

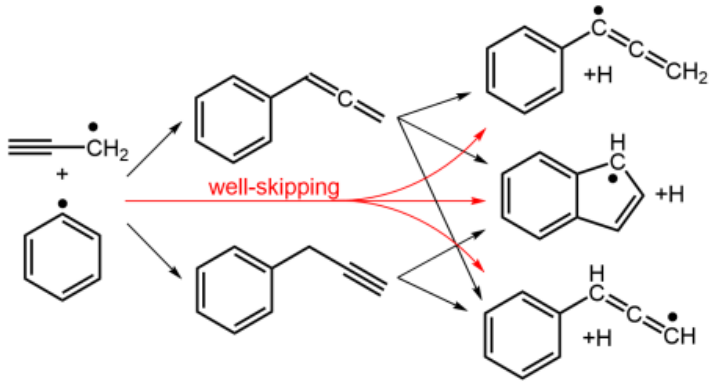
The Phenyl + Benzyl Reaction





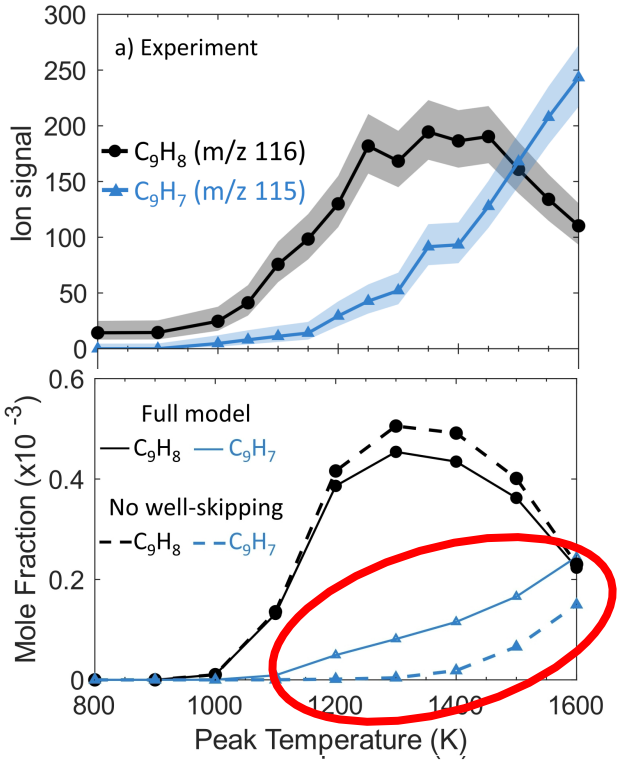
D. E. Couch, A. J. Zhang, C. A. Taatjes, and N. Hansen,
Angew. Chem. Int. Ed., **2021,** 60, 27230-27235

The Phenyl + Propargyl Reaction



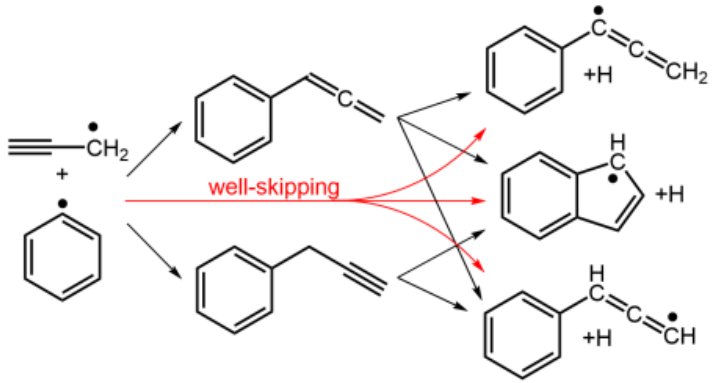
- We cut well-skipping from the simulation
- C_9H_7 yield changes, no longer agrees with experiment

- Conclusion – well-skipping is the dominant source of C_9H_7 here
  - Though C_9H_8 yield is higher

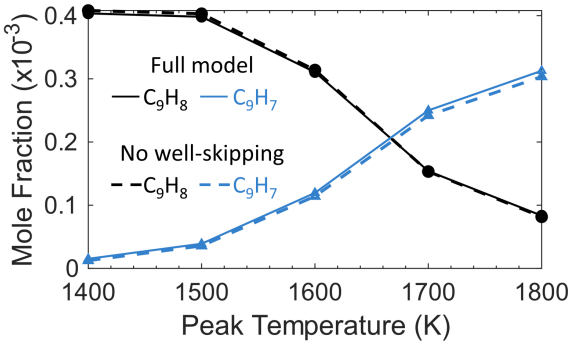


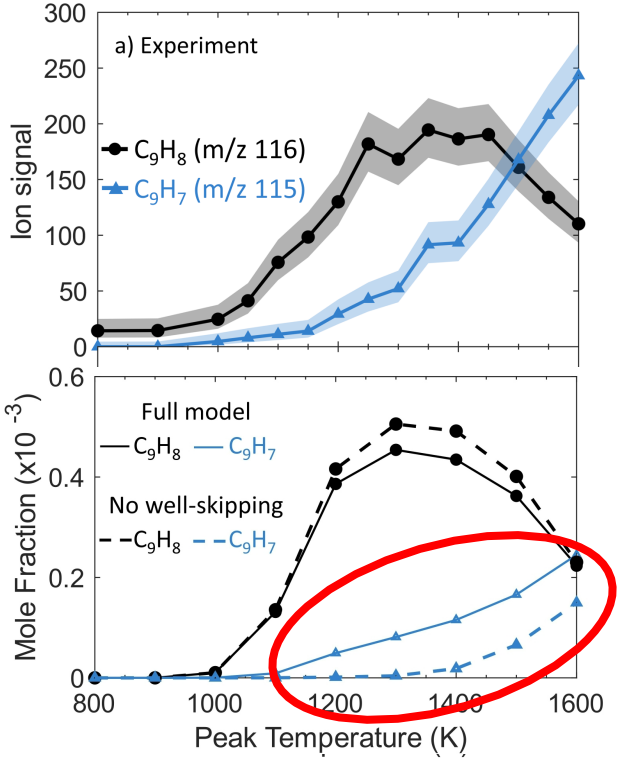
D. E. Couch, G. Kukkadapu, A. J. Zhang, A. W. Jasper, C. A. Taatjes, N. Hansen, *Proc. Combust. Inst.*, **2022,** accepted for presentation

The Phenyl + Propargyl Reaction



- Well-skipping is negligible at atmospheric pressure





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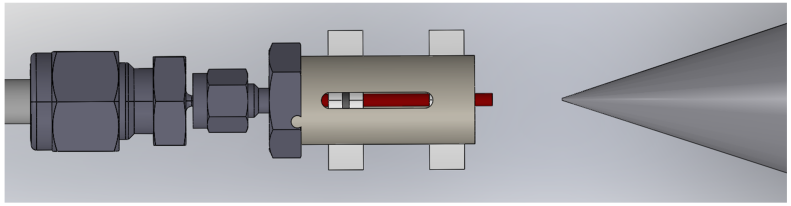
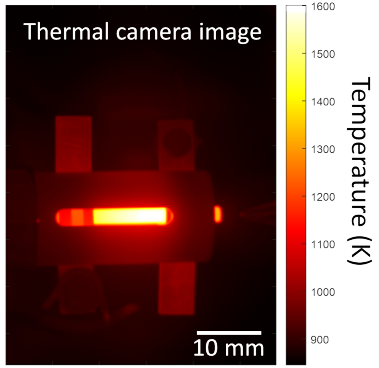
D. E. Couch, G. Kukkadapu, A. J. Zhang, A. W. Jasper, C. A. Taatjes, N. Hansen, *Proc. Combust. Inst.*, **2022,** accepted for presentation

Possible next steps





- Different reactor materials to allow measurements in oxidizing environments
- Application of tandem mass spectrometric diagnostics for more detailed speciation

GAS PHASE CHEMICAL PHYSICS

Acknowledgements

Rebecca Caravan (Argonne)
Ahren Jasper (Argonne)
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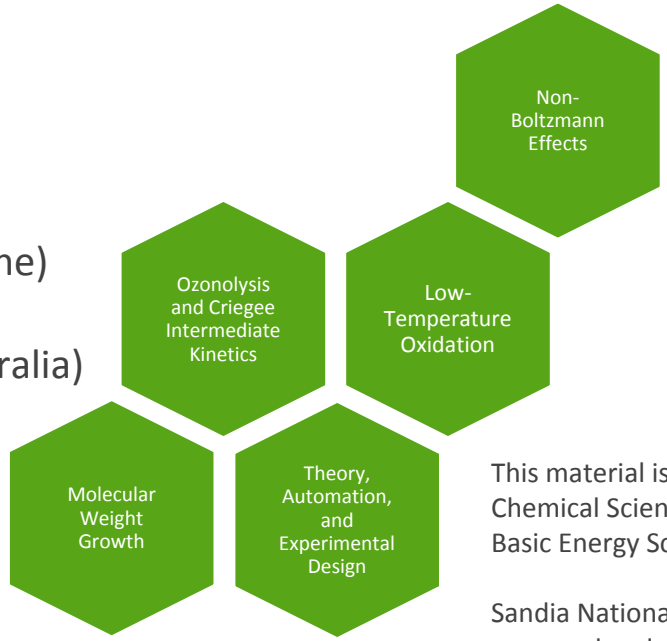
Marsha Lester (Penn)
Carl Percival (JPL)
Brandon Rotavera (Georgia)
Kevin Wilson (LBNL)
Goutham Kukkadapu (LLNL)
Heinz Pitsch (RWTH Aachen, Germany)



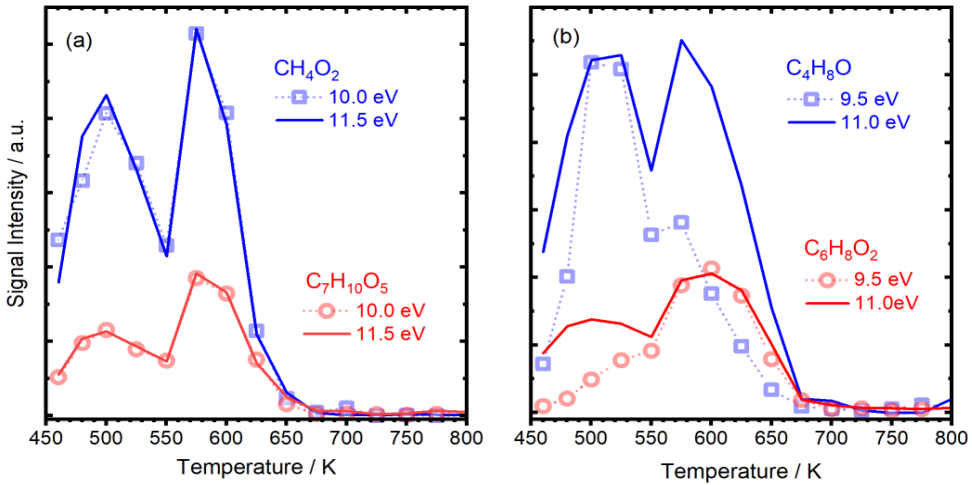
This material is based on work supported by the Office of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, United States Department of Energy.

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Backup Slides

Extreme Low-Temperature Combustion (ELTC):
Ozone-Initiated Oxidation of Methyl Hexanoate

Evidence of differing chemical pathways between ELTC and LTC species are observed

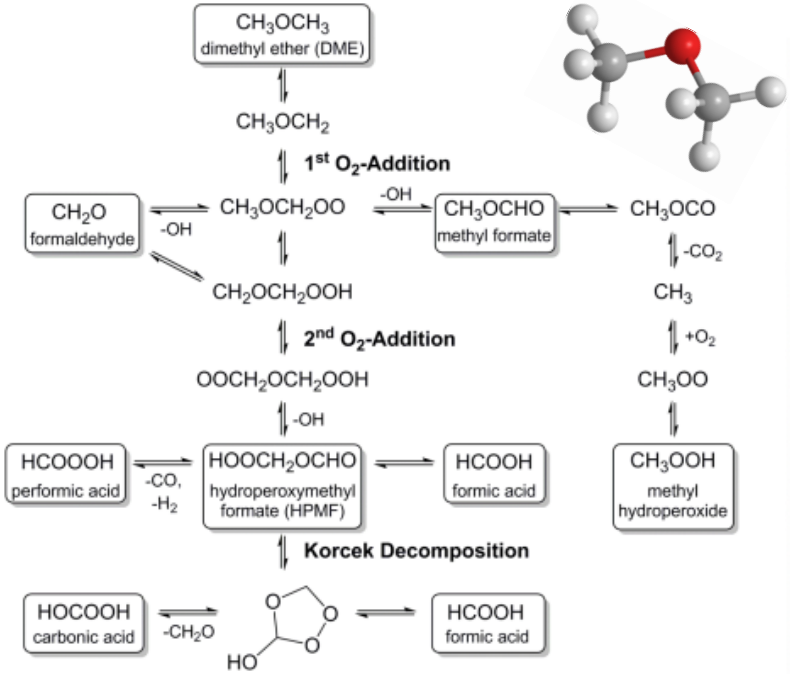


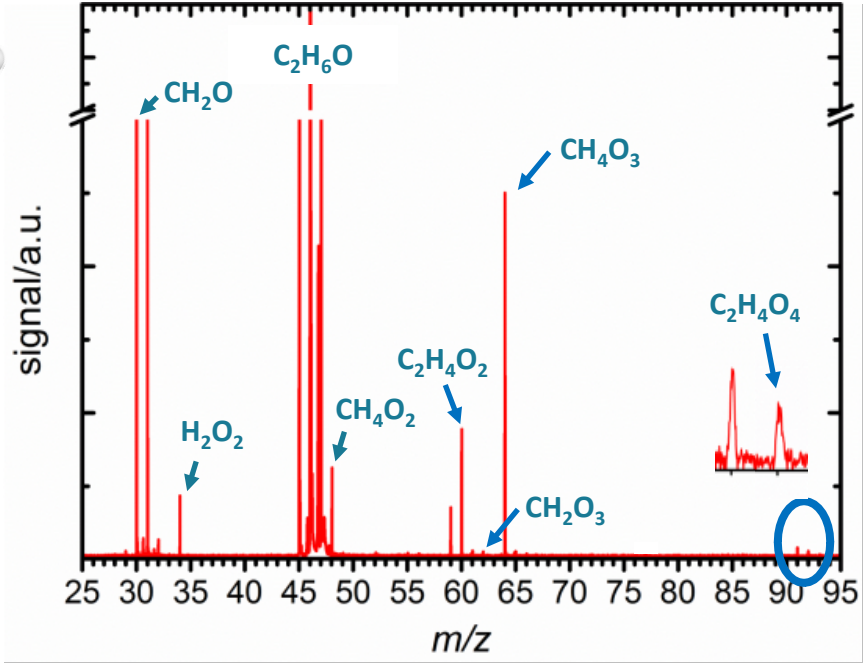
- C_4H_8O and $C_6H_8O_2$ have differing profiles at different ionization energies
  - ✓ Suggests different isomers are appearing in each regime
  - ✓ These species being fragments is unlikely at these lower energies and with larger species – do not match profiles of fuel or major intermediates
- More work and a detailed model are needed to try and identify these species, which is hard with larger molecular structures

GAS PHASE CHEMICAL PHYSICS

A. Rousso *et al., J. Phys. Chem. A,* **2020,** 124, 9897-9914
Invited Feature Article, ACS Editors' Choice, Open Access

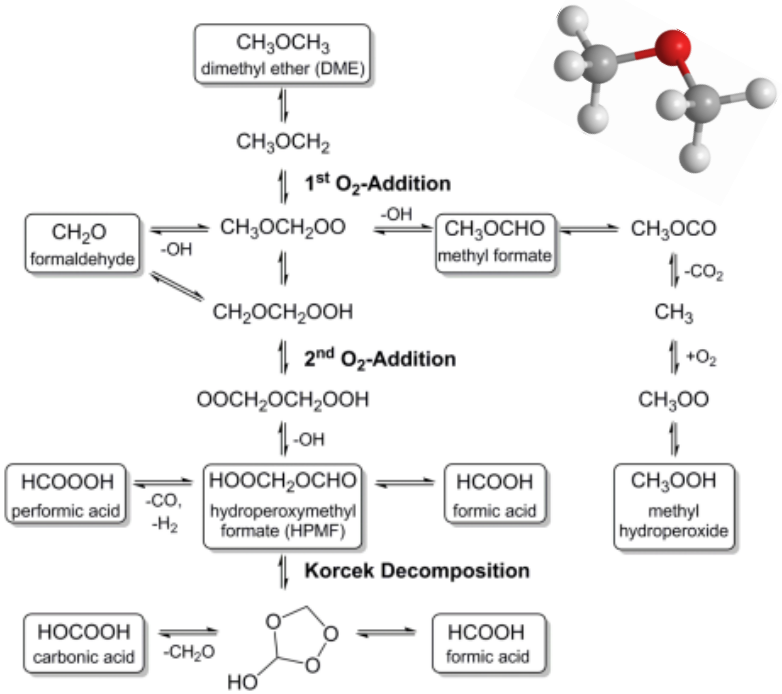
Low-Temperature Oxidation Chemistry of Dimethyl Ether (DME)





K. Moshammer *et al., J. Phys. Chem. A,* **2015,** 119, 7361-7374
K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

Low-Temperature Oxidation Chemistry of Dimethyl Ether (DME)



$CH_3OCH_2 + O_2 \rightleftarrows CH_3OCH_2O_2$ (R1)

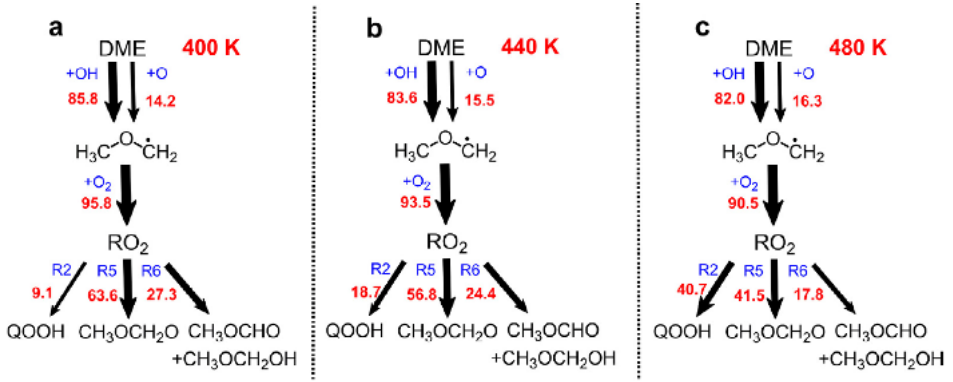
$CH_3OCH_2O_2 \rightleftarrows CH_2OCH_2O_2H$ (R2)

$CH_2OCH_2O_2H + O_2 \rightleftarrows O_2CH_2OCH_2O_2H$ (R3)

$O_2CH_2OCH_2O_2H \rightleftarrows HOOCH_2OCHO + OH$ (R4)

$2\ CH_3OCH_2O_2 \rightleftarrows 2\ CH_3OCH_2O + O_2$ (R5)

$2\ CH_3OCH_2O_2 \rightleftarrows CH_3OCHO + CH_3OCH_2OH + O_2$ (R6)



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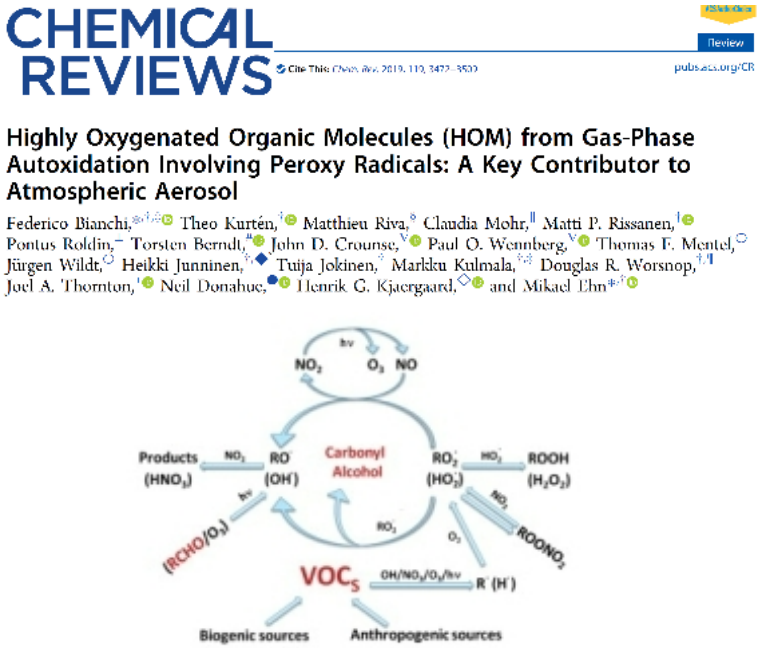
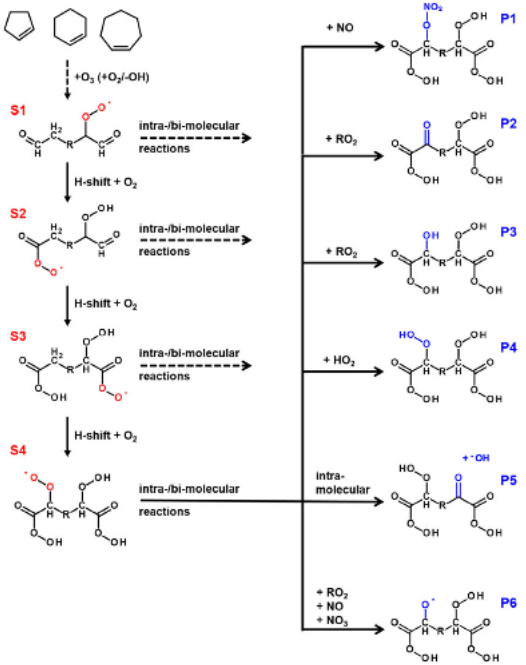
GAS PHASE CHEMICAL PHYSICS

Highly Oxygenated Molecules (HOM):
From Gas-Phase Oxidation to Atmospheric Aerosol





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