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COMBUSTION RESEARCH FACILITY

Analysis of OH and HO_2 Time Histories Measured in Low-Temperature Oxidation of Hexene Isomers

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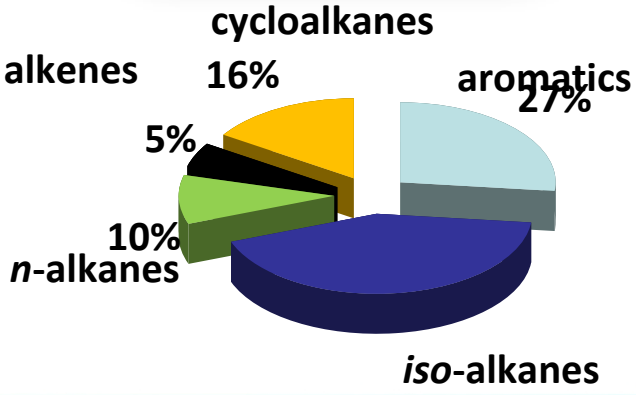
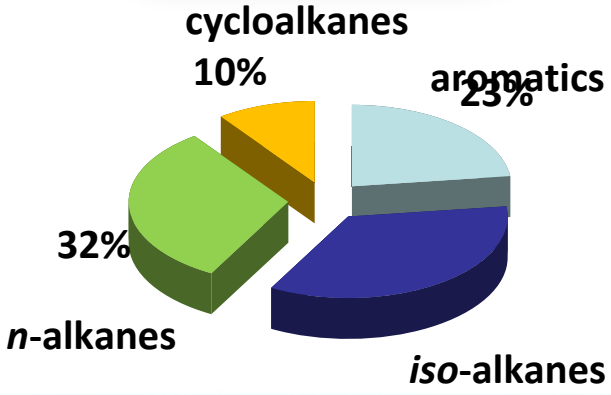
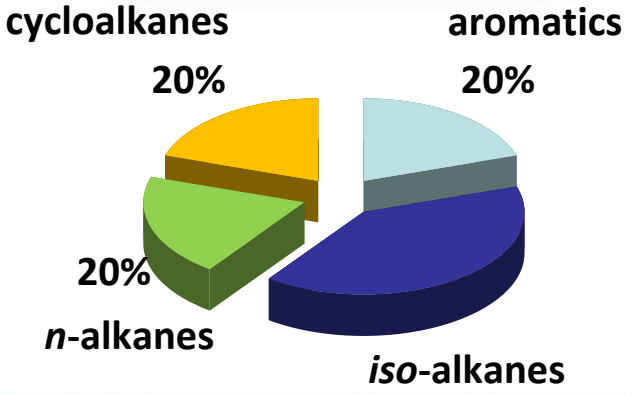
Sandia National Laboratories

Conventional Transportation Fuels Contain Different Distributions of Hydrocarbon Classes, Species

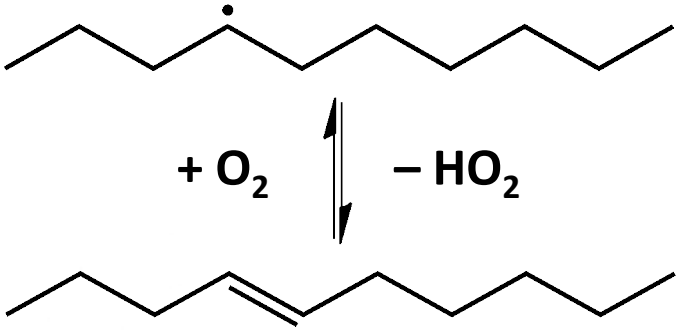
- General requirements for molecular structure of transportation fuels
  - Gasoline: short (< C_8) branched chains, aromatics, high octane number
  - Diesel: long (> C_{12}), straight chains, substituted naphthenes, aromatics
  - Jet Fuel: long (> C_9), straight chains, *iso*-alkanes, aromatics

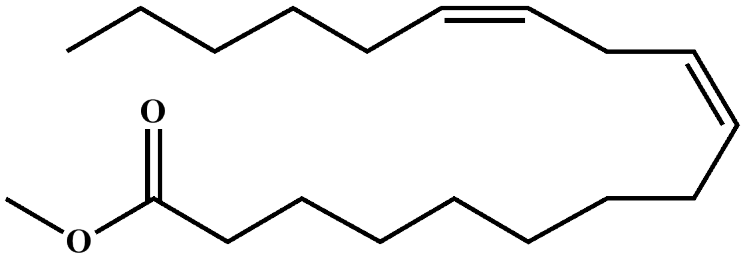


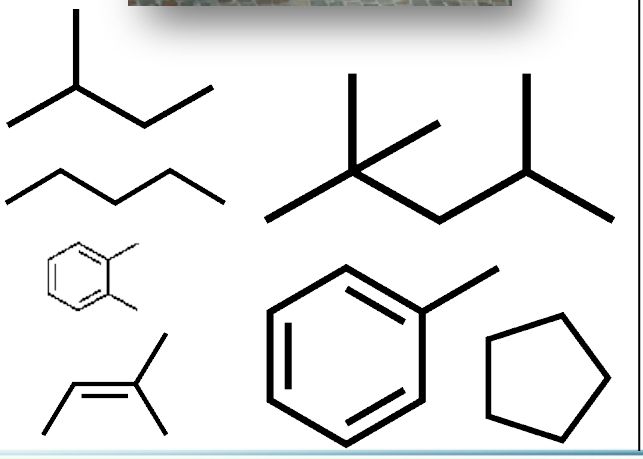


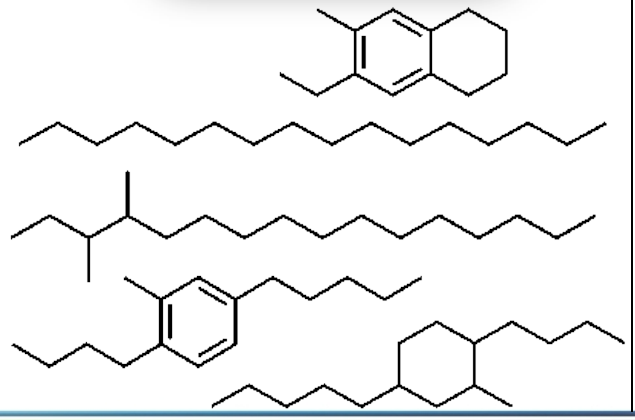


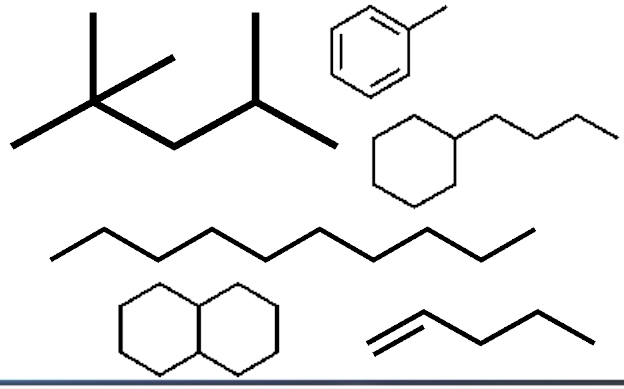
C=C Bonds Relevant to Conventional Fuels, Biofuels



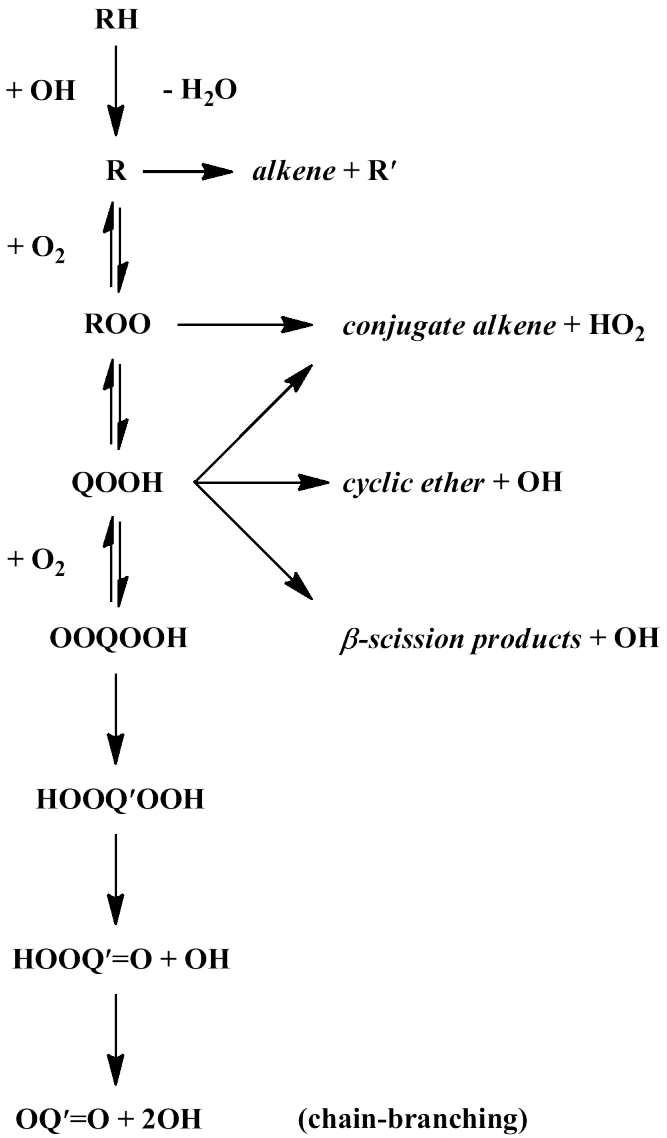








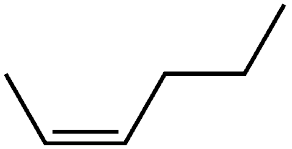
Motivation: Study the Influence of C=C Position on Low-Temperature Autoignition Chemistry using Hexene



1-hexene

2-hexene

(E)



(Z)

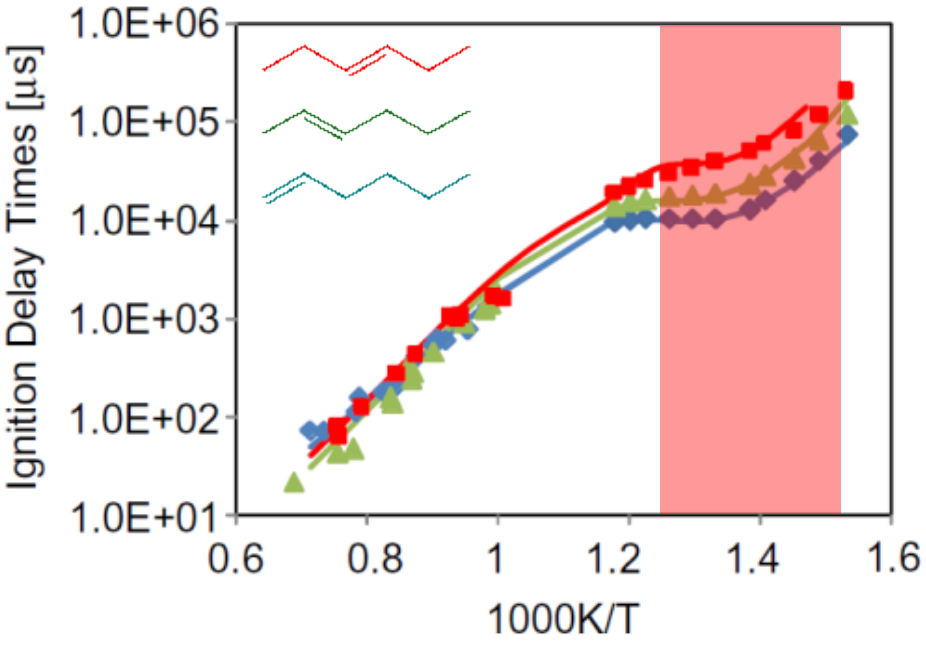
3-hexene

(E)

(Z)

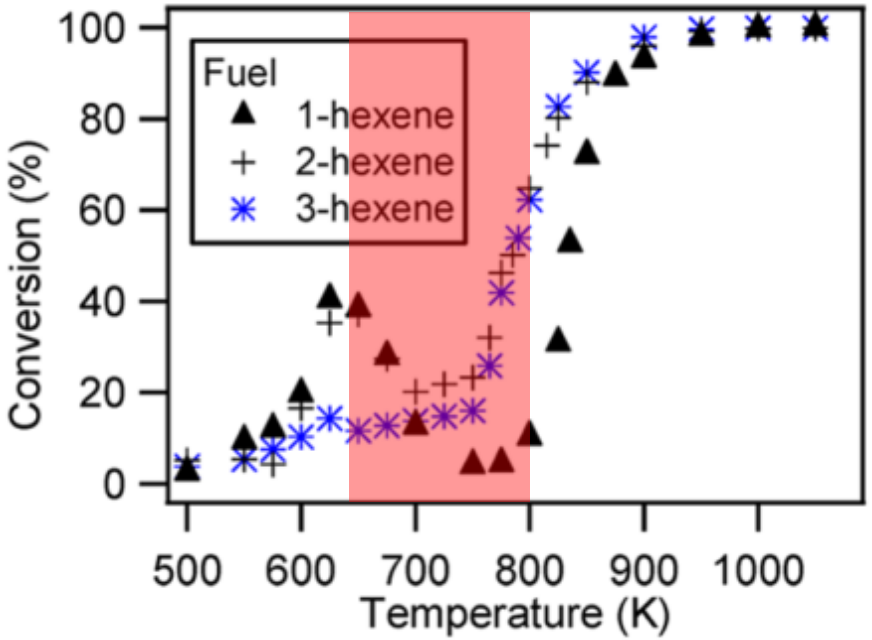
Differing Isomer-Specific Reactivities Observed in RCM, JSR

800 K – 650 K



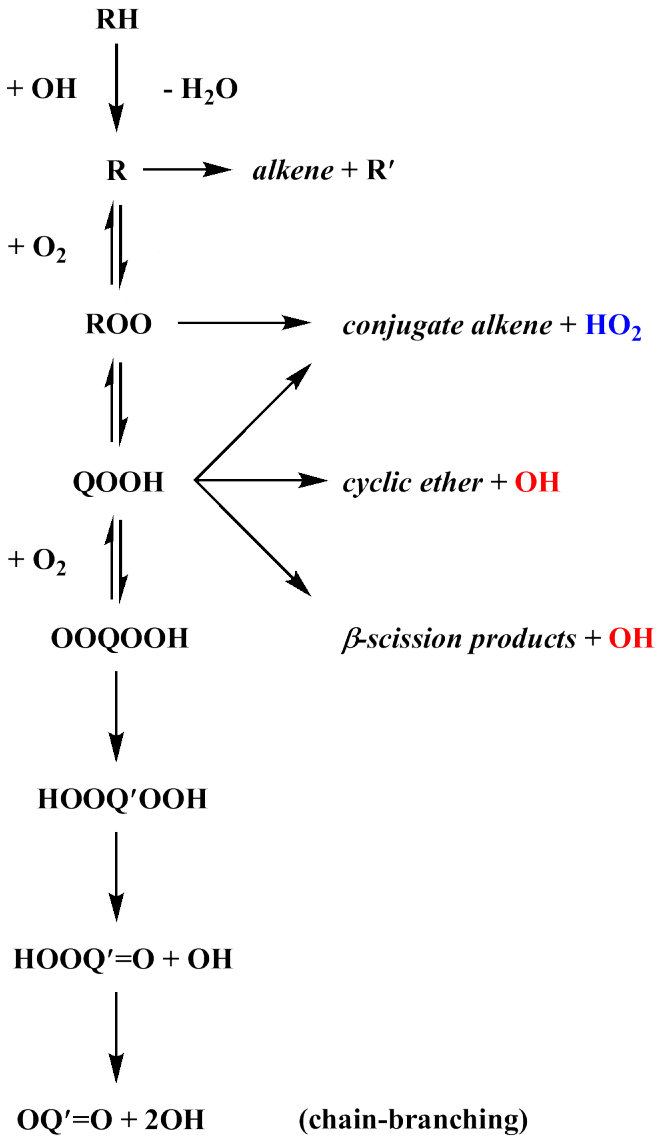
RCM Ignition Times (< 1000 K)
Vanhove et al.
Proc. Comb. Inst., 2005
8 atm, 2.3% (vol.) RH

650 K – 800 K



JSR Speciation
Battin-Leclerc et al.
J. Phys. Chem. A, 2014
1 atm, 1.0% (vol.) RH

Alkene Oxidation Requires Accounting for Additional Reaction Sequences Compared to Alkane Oxidation



RH + HO_2 ⟶ QOOH* ⟶ oxirane + OH or RO_2

⟶ saturated cyclic ethers + OH

R′ + HO_2 ⟶ RO_2H ⟶ RO + OH

(delayed chain-branching)

RH + OH ⟶ Waddington (carbonyl + OH)

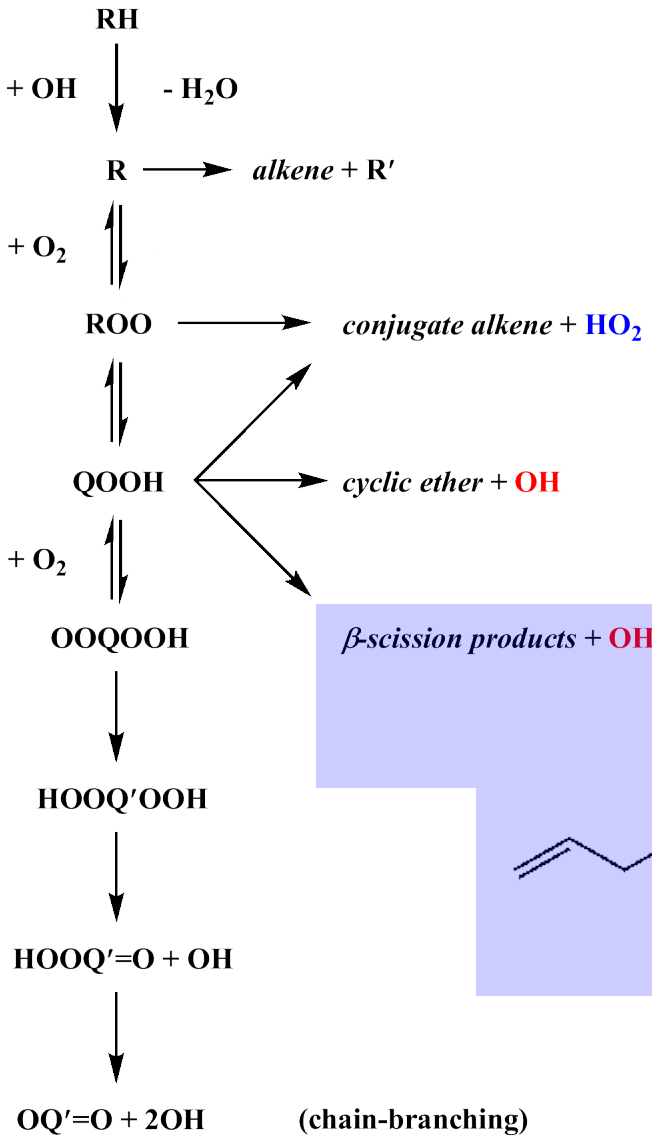
⟶ OH-substituted cyclic ether + OH

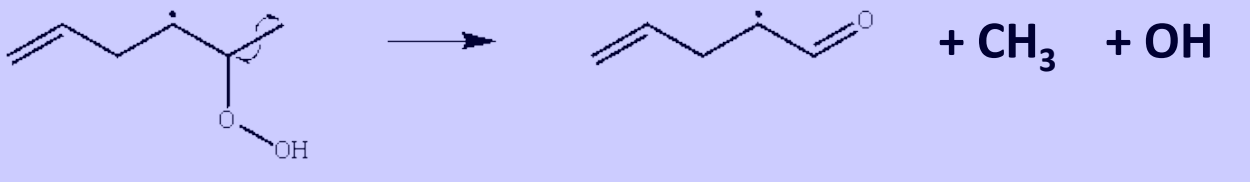
R + O_2 ⟶ QOOH ⟶ cyclic ether* + OH

*unsaturated chain + OH

*C=C bond in ring + OH

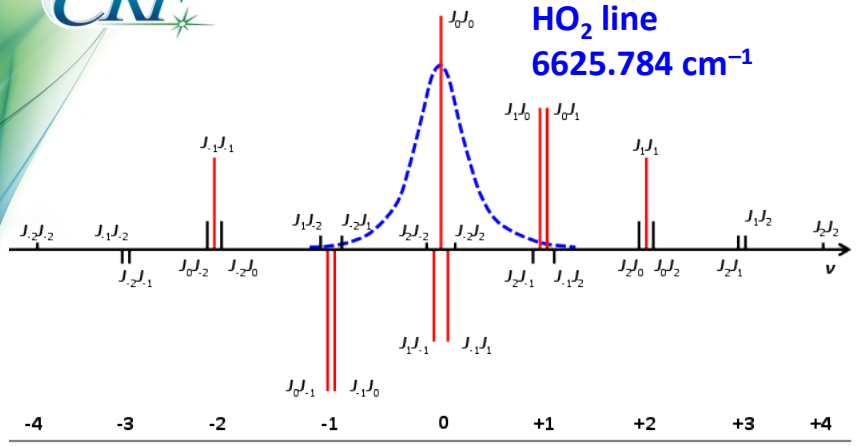
Alkene Oxidation Requires Accounting for Additional Reaction Sequences Compared to Alkane Oxidation

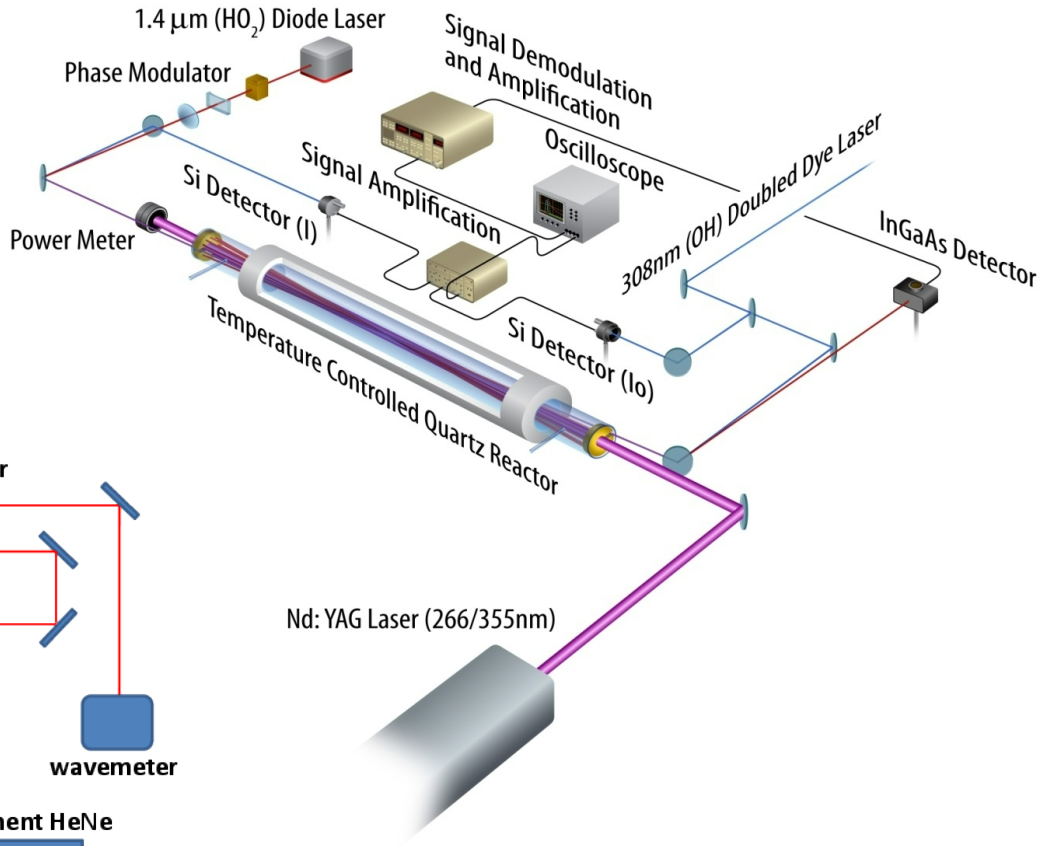


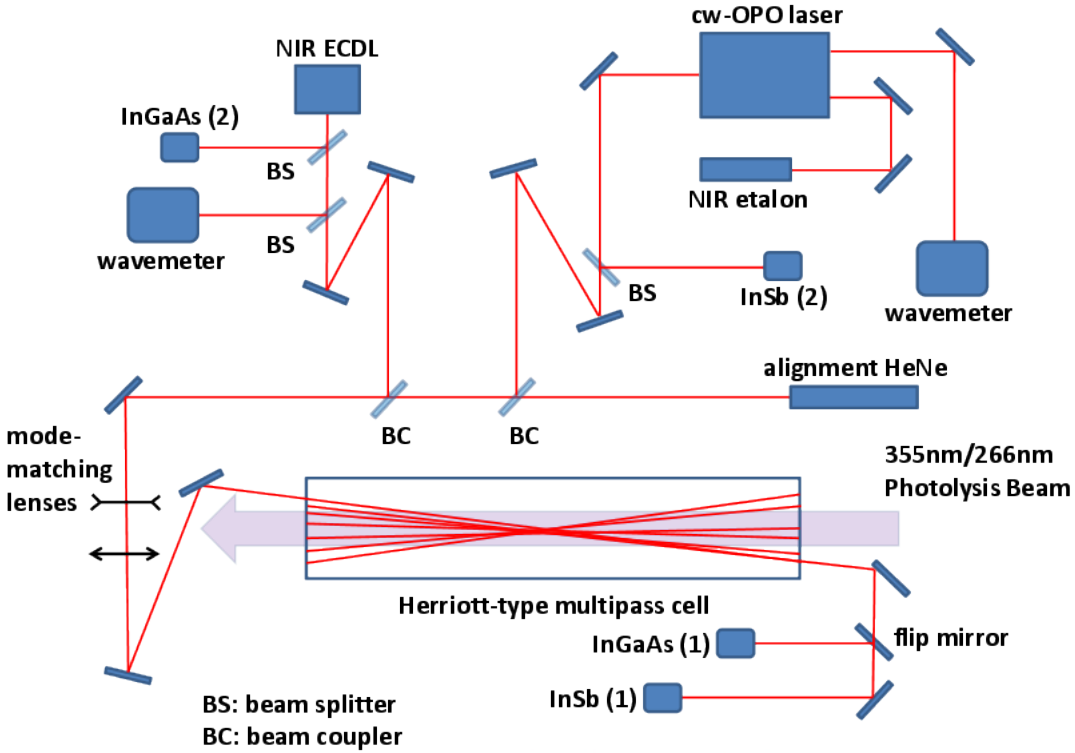


Experimental Details

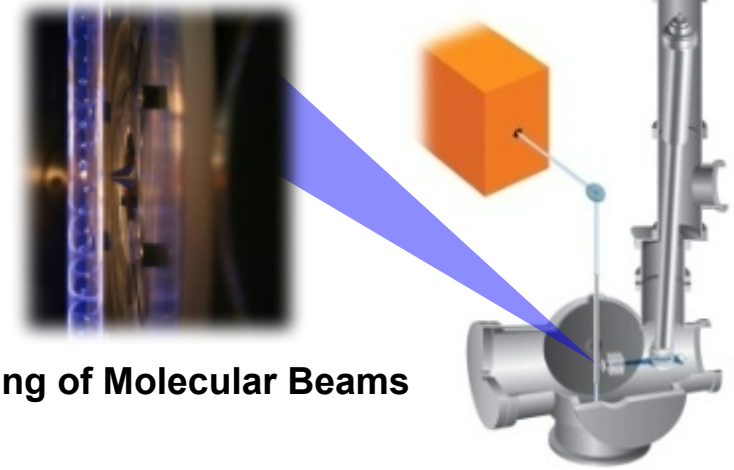
Multi-pass Infrared-Absorption Experiment



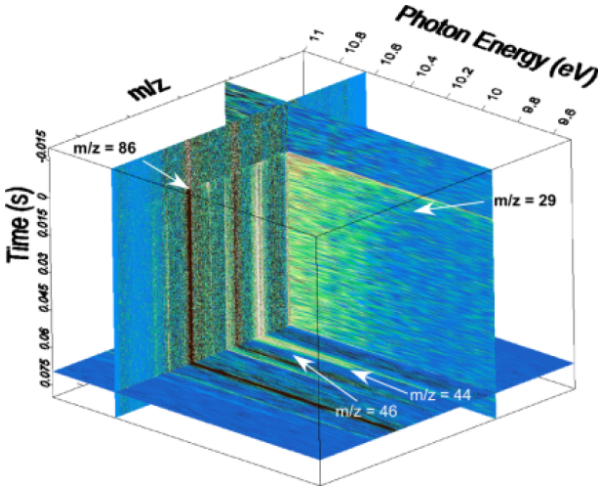




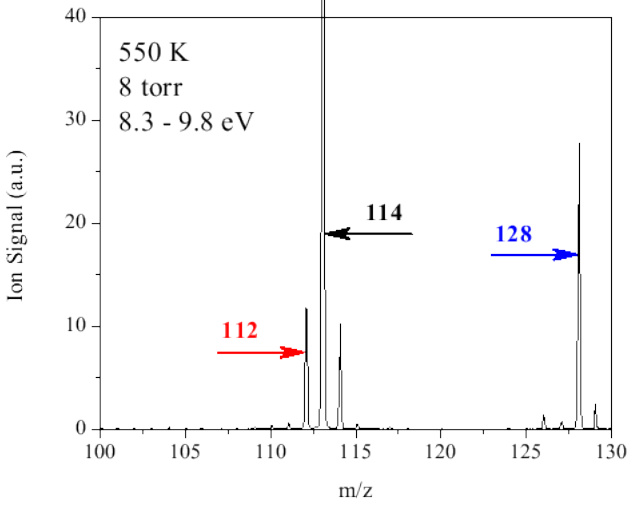
Intermediates from Oxidation Reactions Probed using VUV Photoionization of Molecular Beams



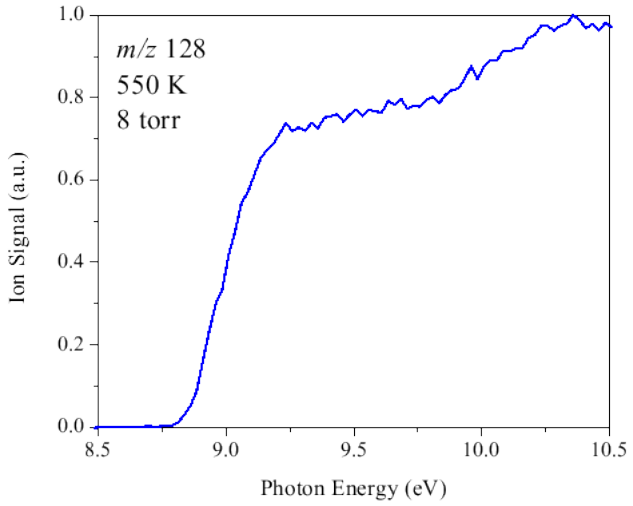
Probing of Molecular Beams



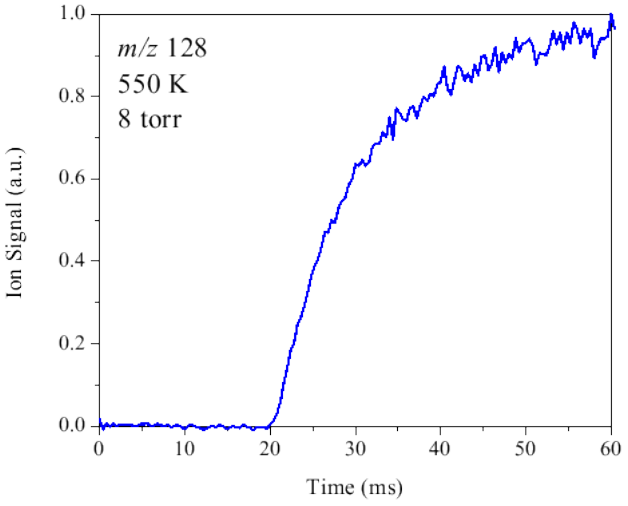
High-Resolution Mass Spectra



Isomer-Resolved Species Identification



Time-Dependent Chemical Kinetics



Conditions for Cl-Initiated Oxidation Experiments

Multi-pass Infrared-Absorption (IR) Conditions

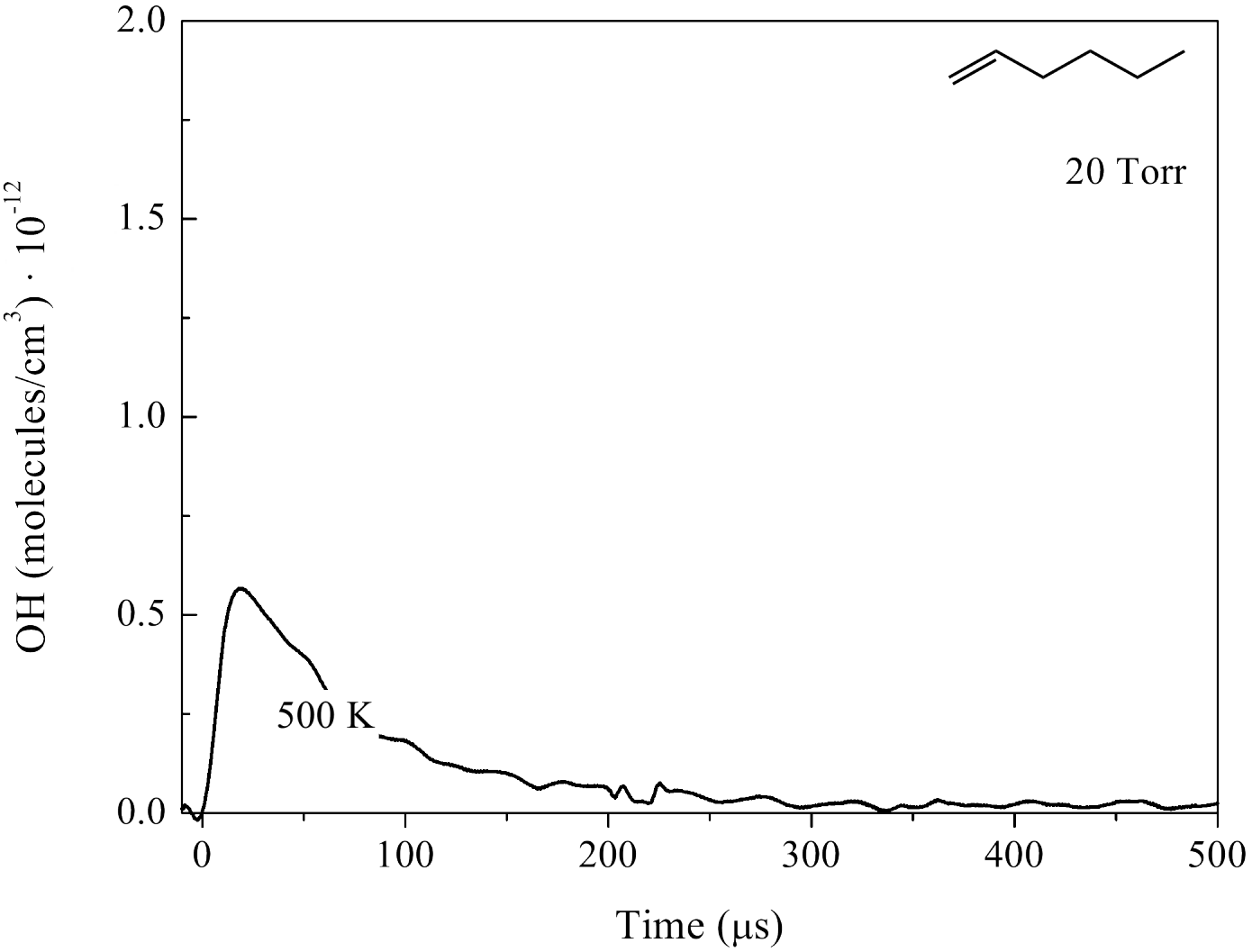
Species	*Number Density (molecules/cm^3)*	
Hexene	$1.9 \cdot 10^{15}$	
O_2	$4.1 \cdot 10^{16}$	500 – 750 K
Cl (photolyzed Cl_2)	$3.4 \cdot 10^{13}$	20 Torr
He	$3.4 \cdot 10^{17}$	

Multiplexed Photoionization Mass Spectrometry (MPIMS) Conditions

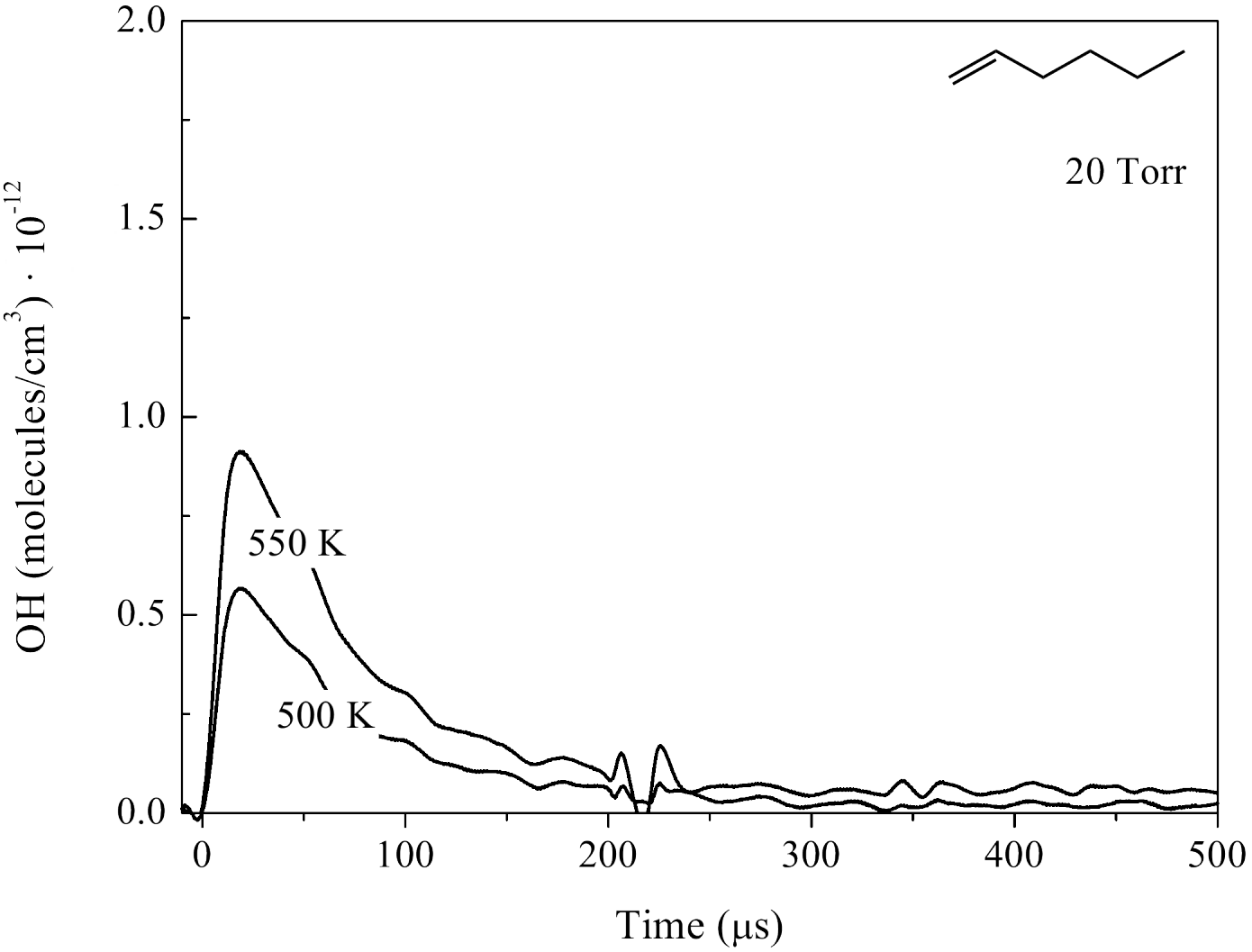
Species	*Number Density (molecules/cm^3)*	
Hexene	$7.0 \cdot 10^{13}$	
O_2	$1.4 \cdot 10^{16}$	550 K
Cl (photolyzed OxCl)	$4.4 \cdot 10^{12}$	8 Torr
He	$4.9 \cdot 10^{16}$	

OH Time History Results

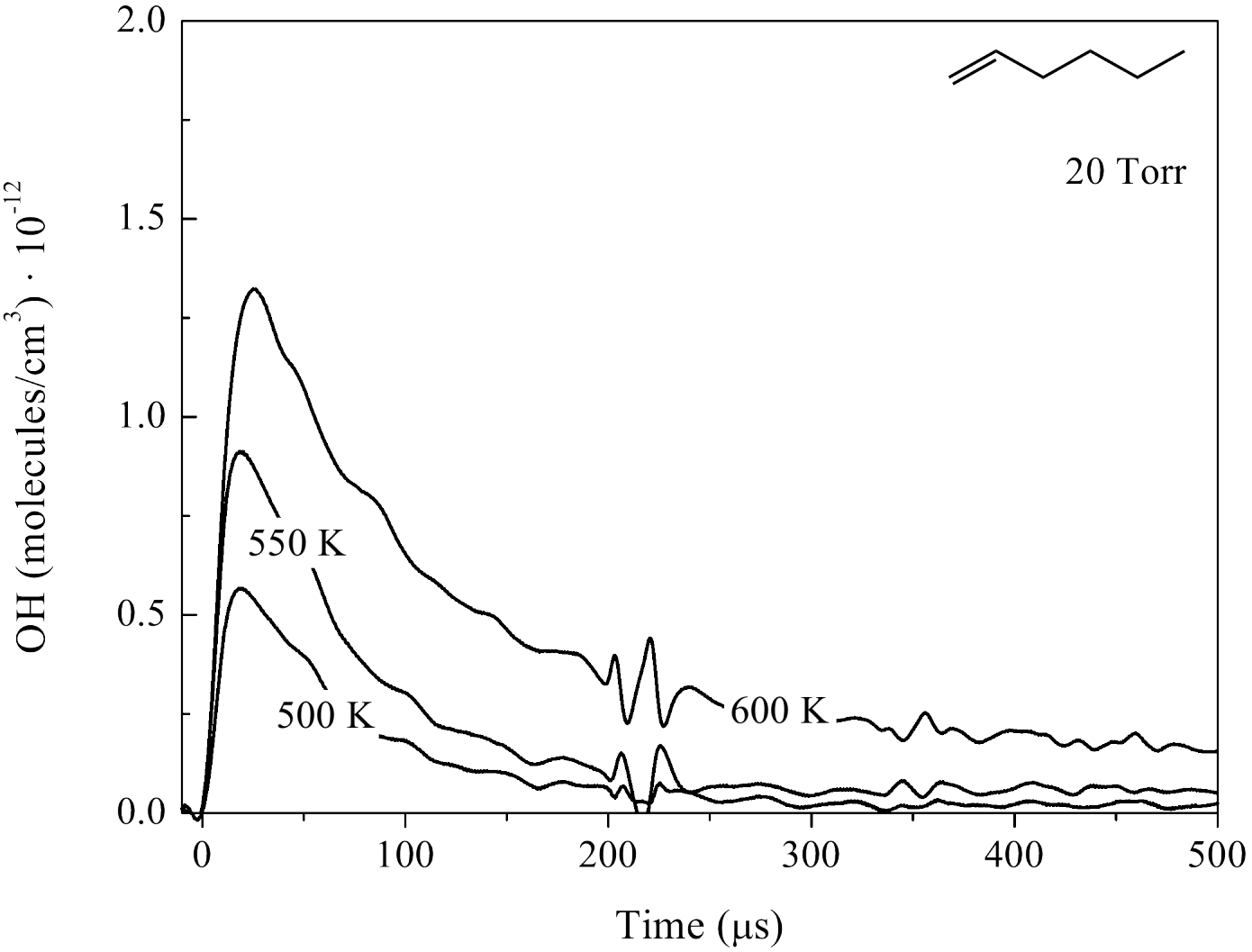
OH Time Histories of 1-Hexene



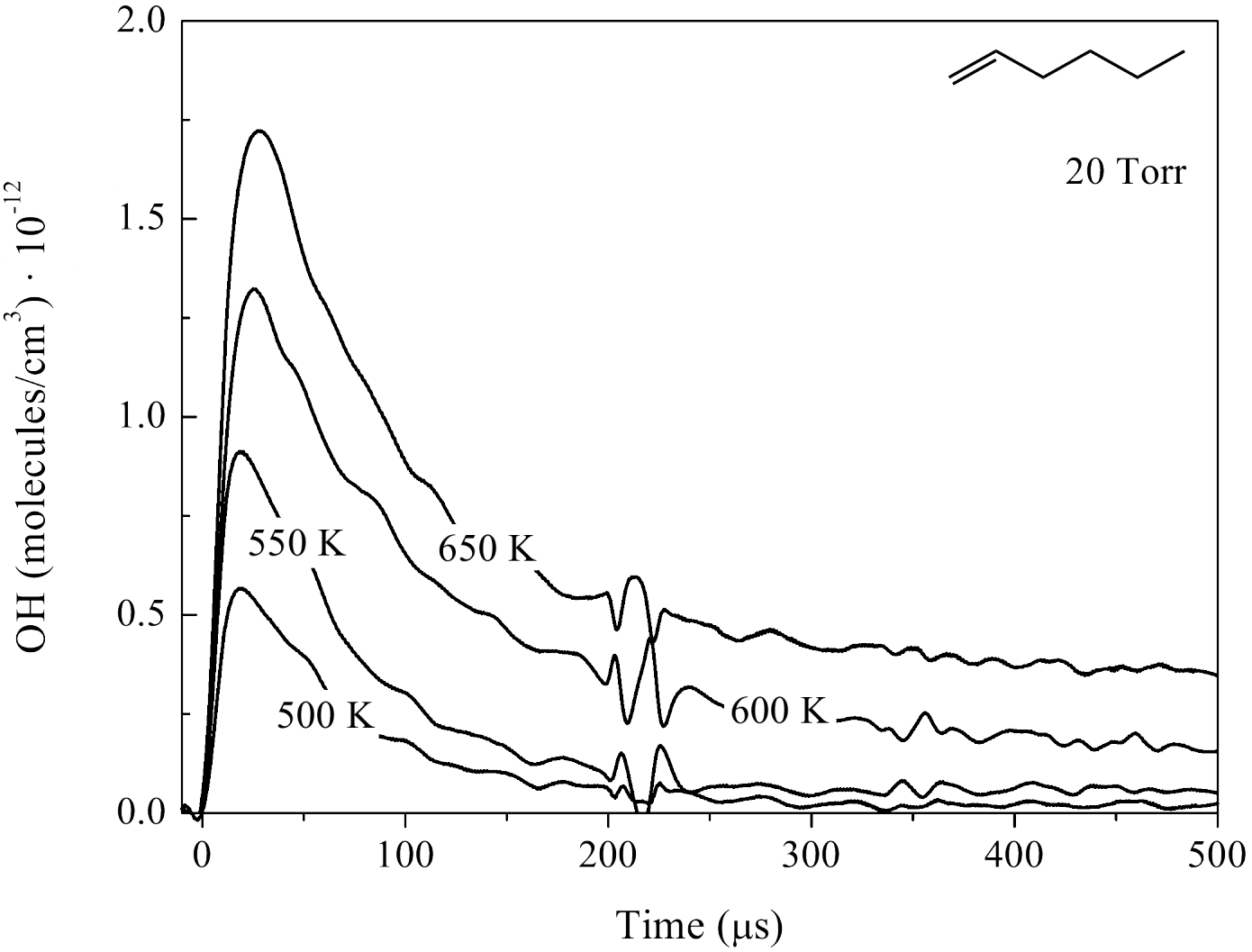
OH Time Histories of 1-Hexene



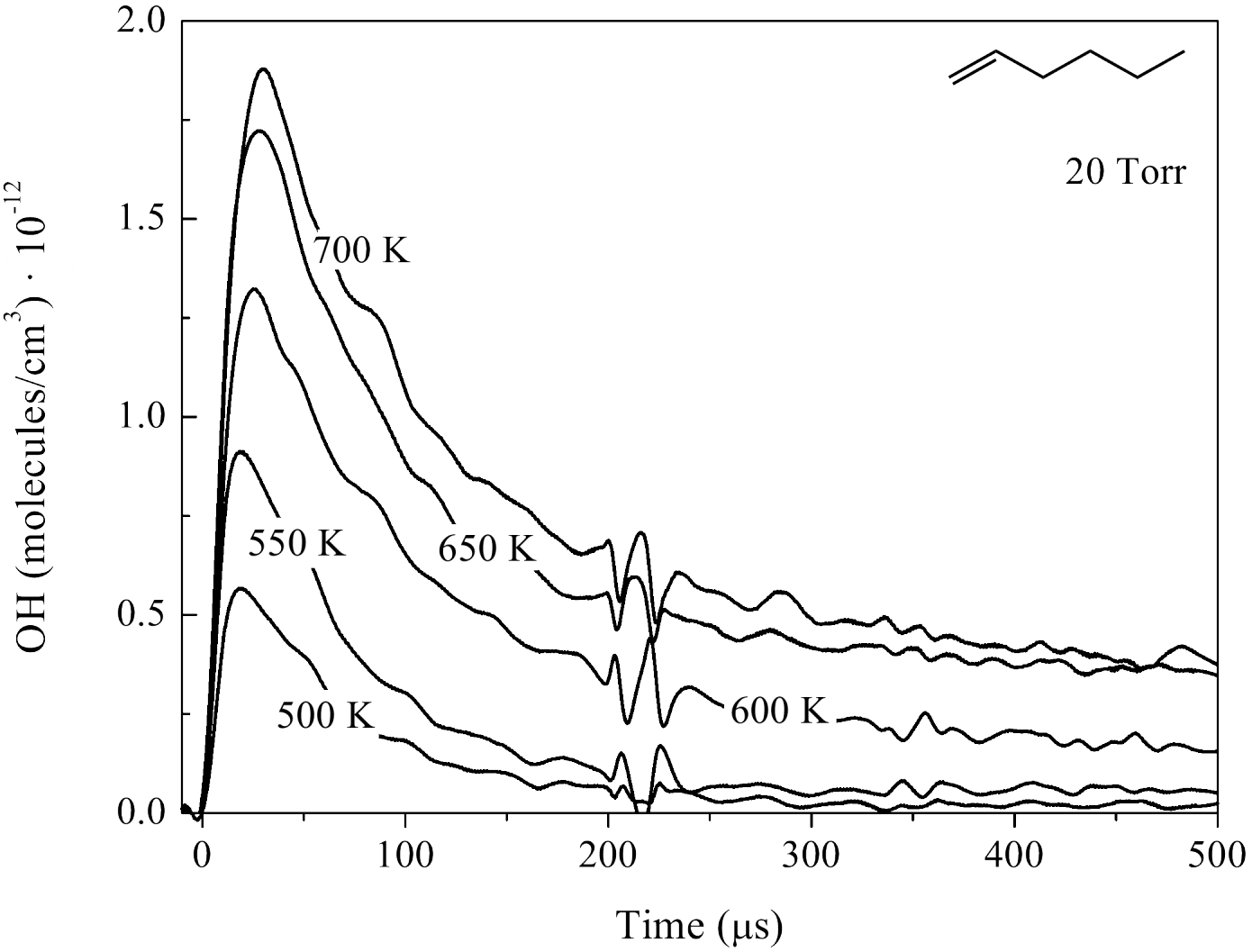
OH Time Histories of 1-Hexene



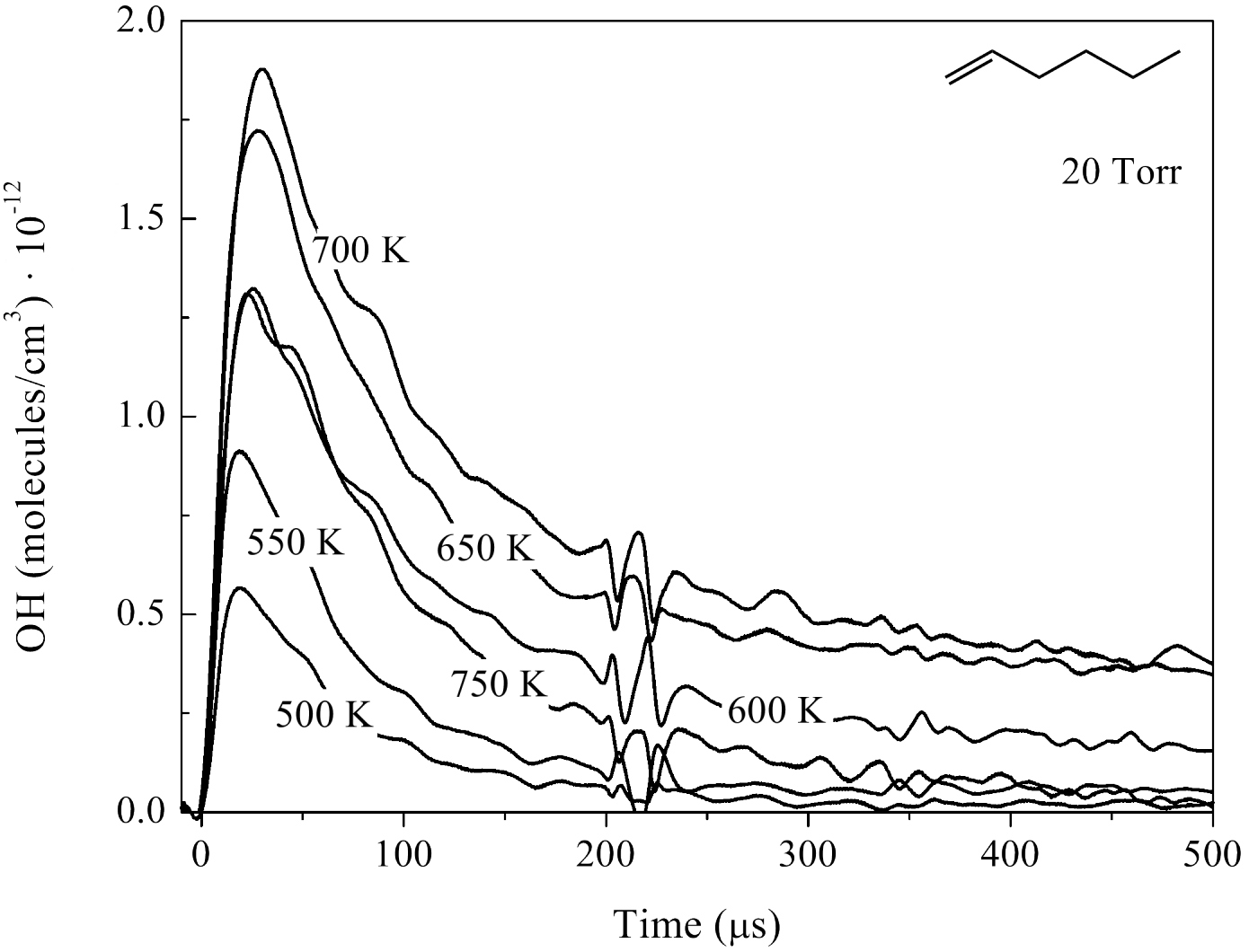
OH Time Histories of 1-Hexene



OH Time Histories of 1-Hexene



OH Time Histories of 1-Hexene

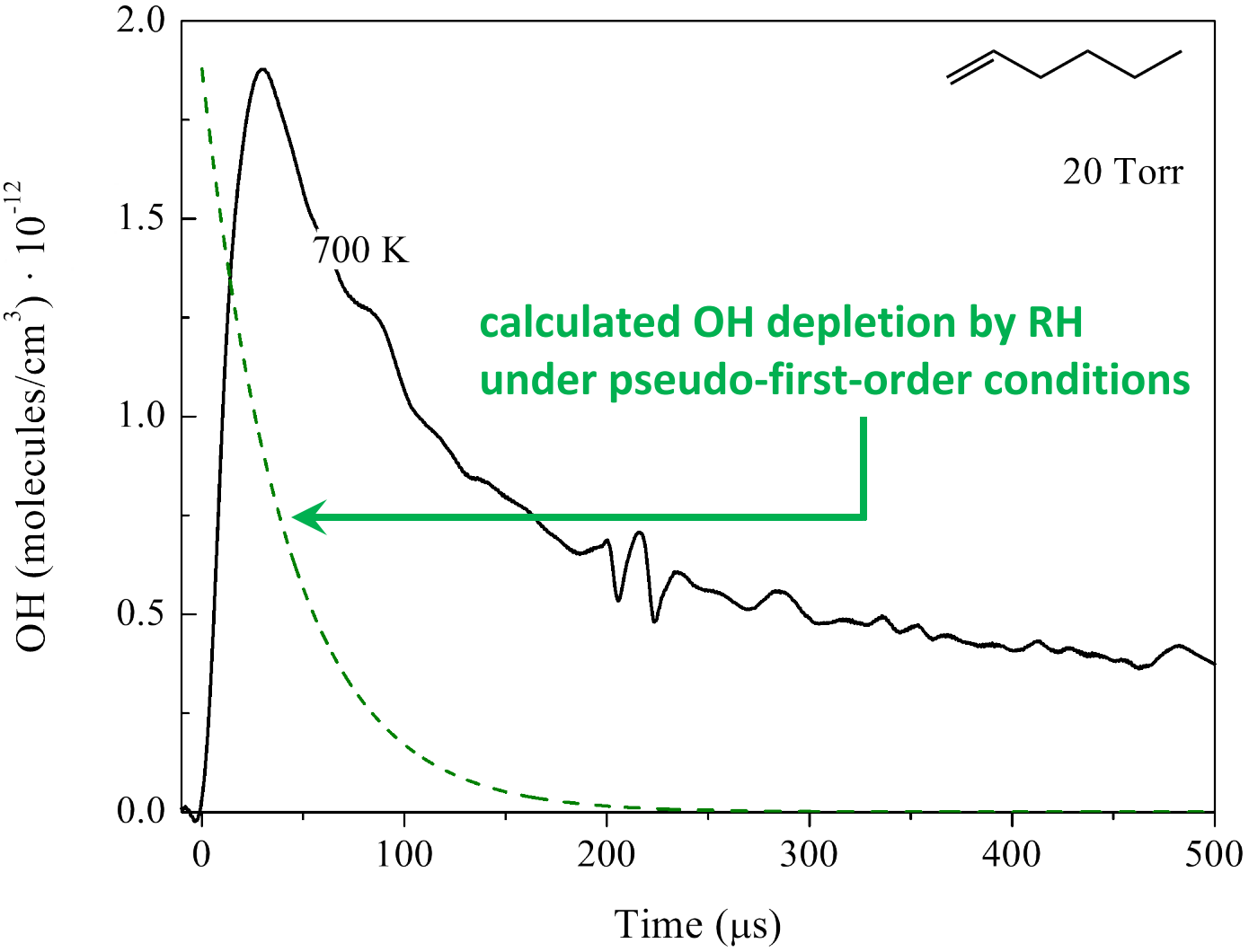


OH Consumption Reactions by 1-Hexene – Rate Parameters from LLNL n-Alkane Model (2011)

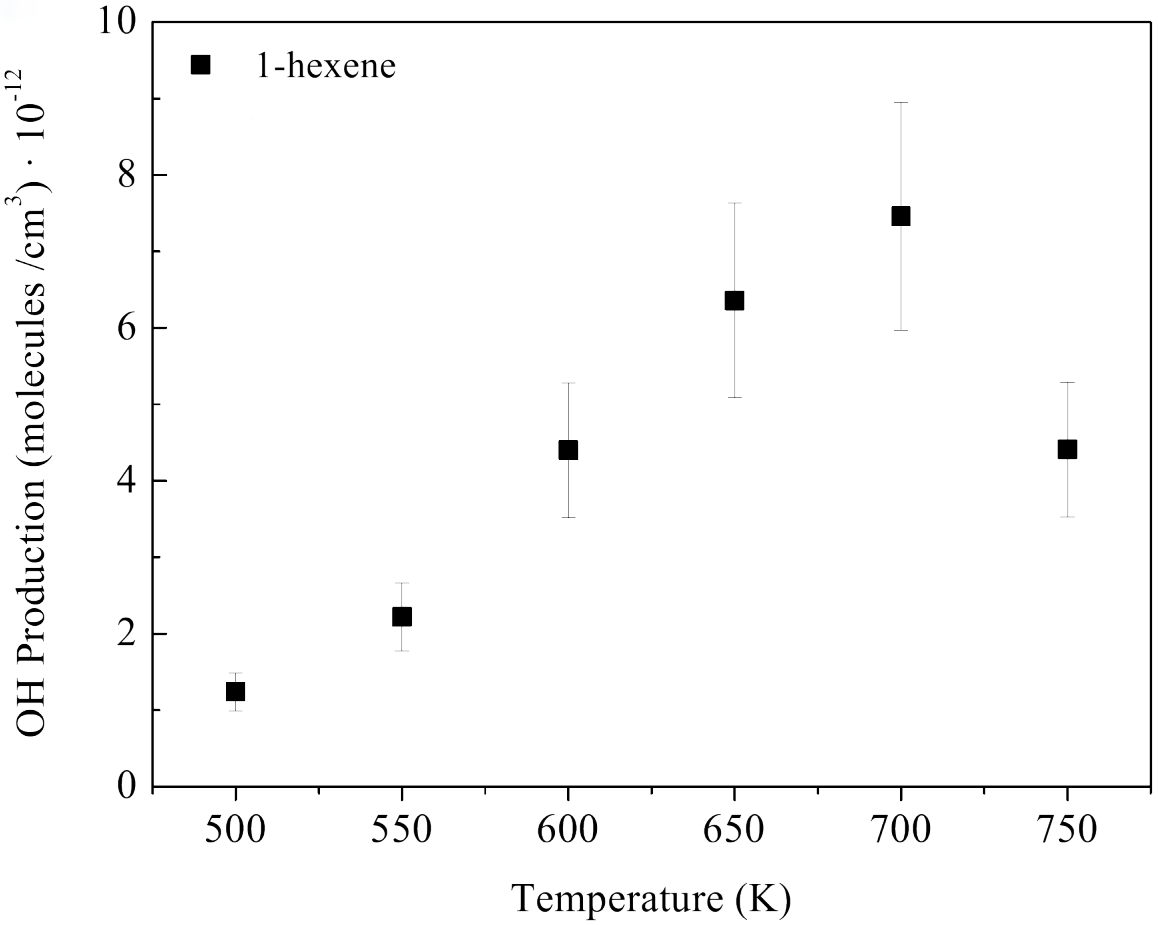
Reaction	A	n	E_a (kcal/mol)
c6h12-1 + oh<=>c5h11-1+ch2o	1.000e+11	0.00	-4.000e+03
c6h12-1 + oh<=>c6h111-3+h2o	2.764e+04	2.64	-1.919e+03
c6h12-1 + oh<=>c6h111-4+h2o	4.670e+07	1.61	-3.500e+01
c6h12-1 + oh<=>c6h111-5+h2o	4.670e+07	1.61	-3.500e+01
c6h12-1 + oh<=>c6h111-6+h2o	5.270e+09	0.97	1.586e+03
c6h12-1 + oh<=>c6h12oh-1	1.000e+12	0.00	-1.042e+03

dominant loss channel of OH:
OH + RH ⟶ products

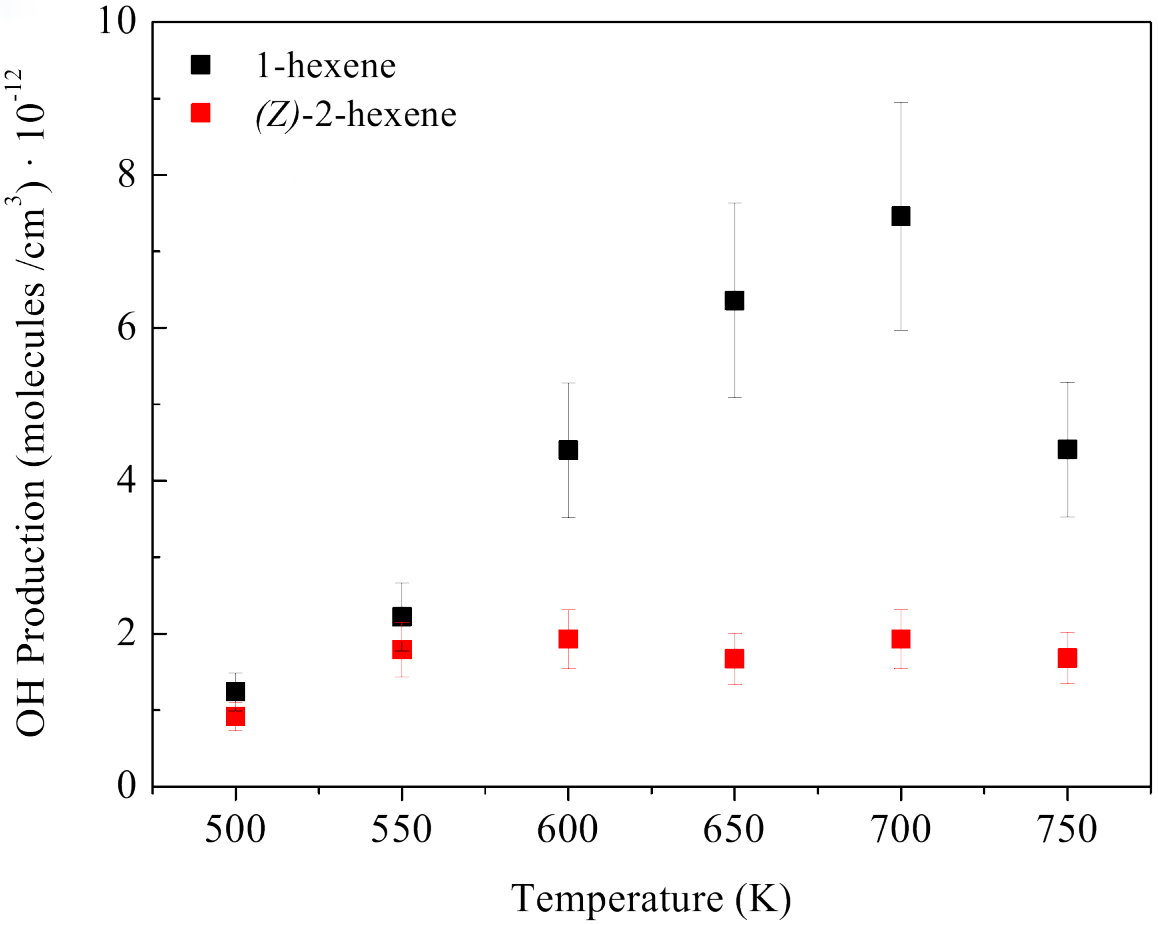
OH Time History from 1-Hexene Oxidation at 700 K, Calculated Pseudo-First-Order OH Consumption by RH

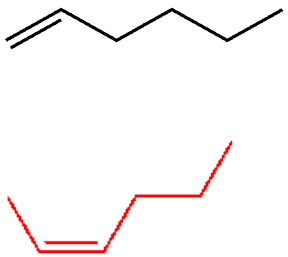


Integrated OH Formation from Oxidation of 1-Hexene

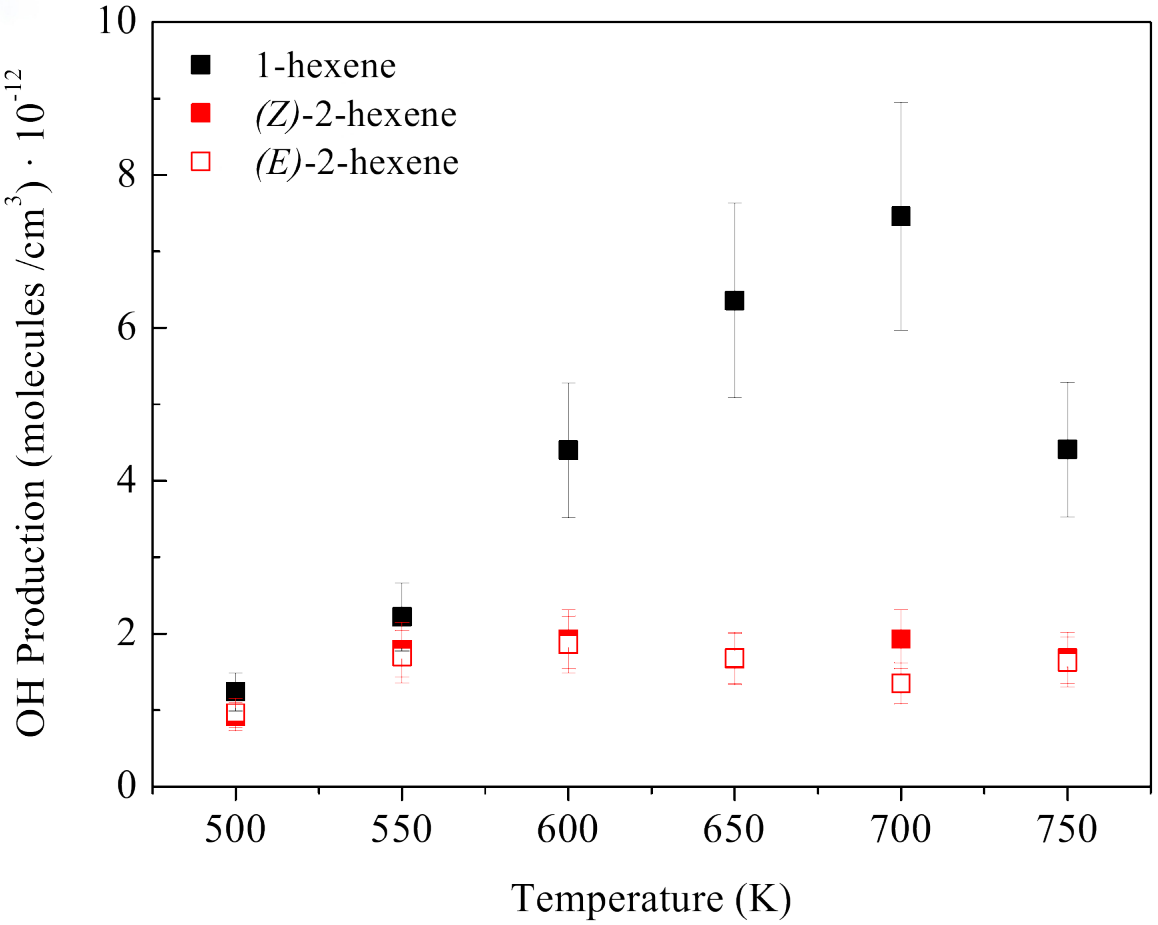


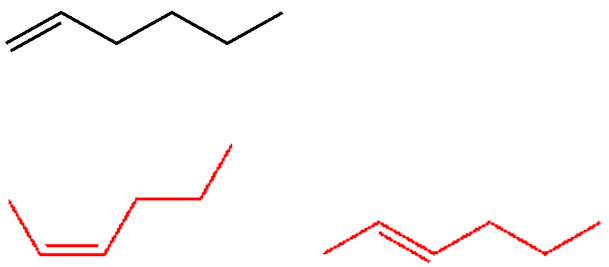
Integrated OH Formation from Oxidation of 1-Hexene, *(Z)*-2-Hexene



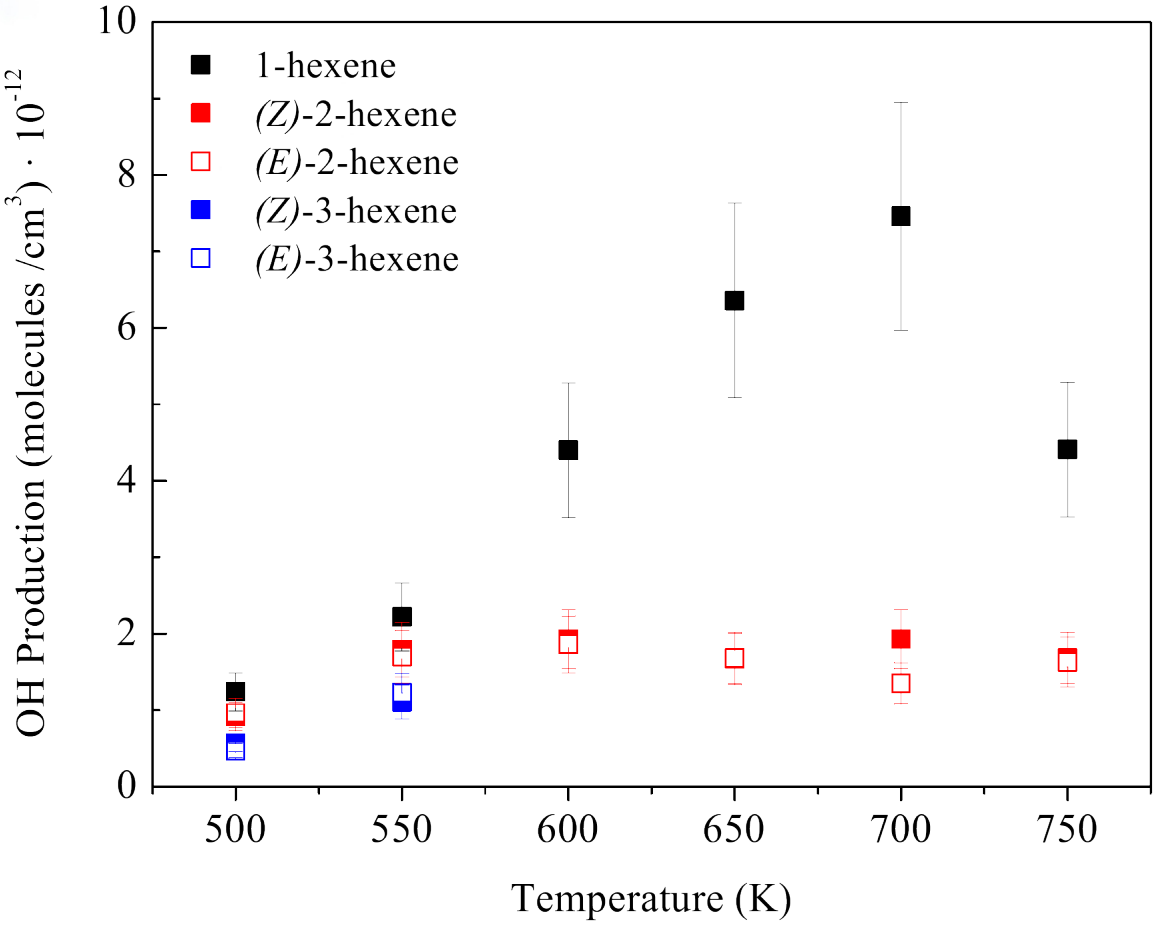


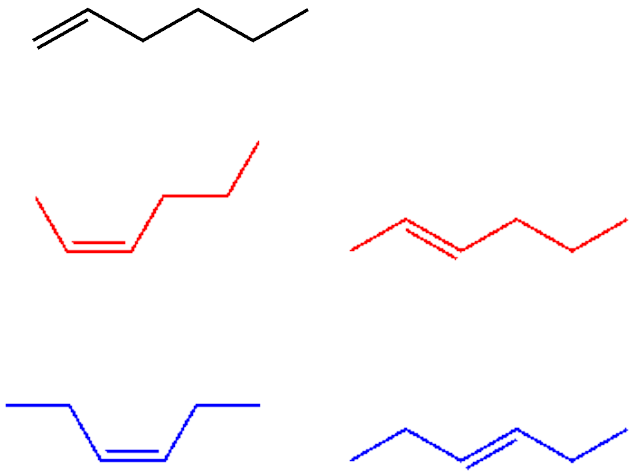
Integrated OH Formation from Oxidation of 1-Hexene, *(Z)*-2-Hexene, *(E)*-2-Hexene





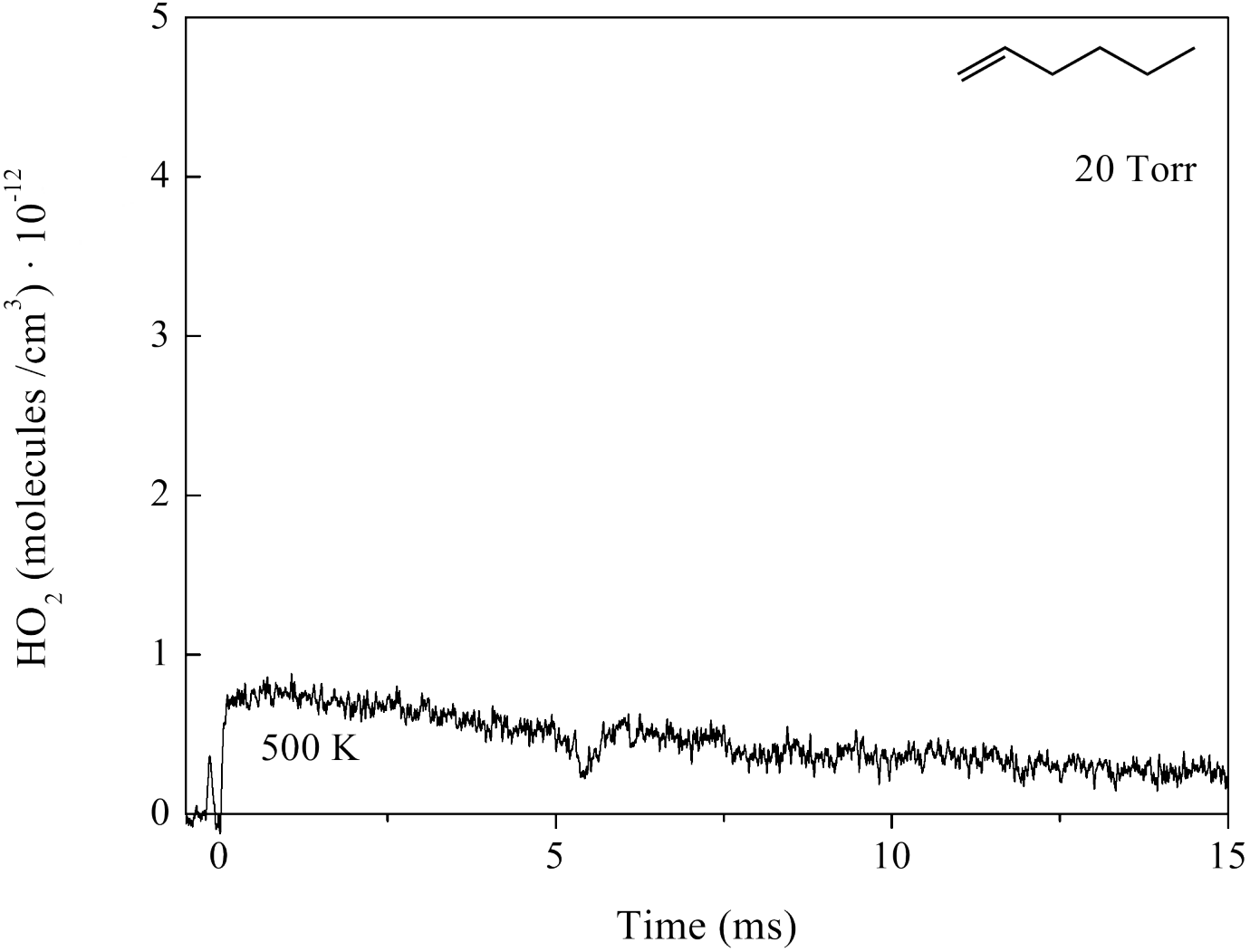
Integrated OH Formation from Oxidation of 1-Hexene, *(E)*-2-Hexene, *(Z)*-2-Hexene, *(Z)*-3-Hexene, *(E)*-3-Hexene



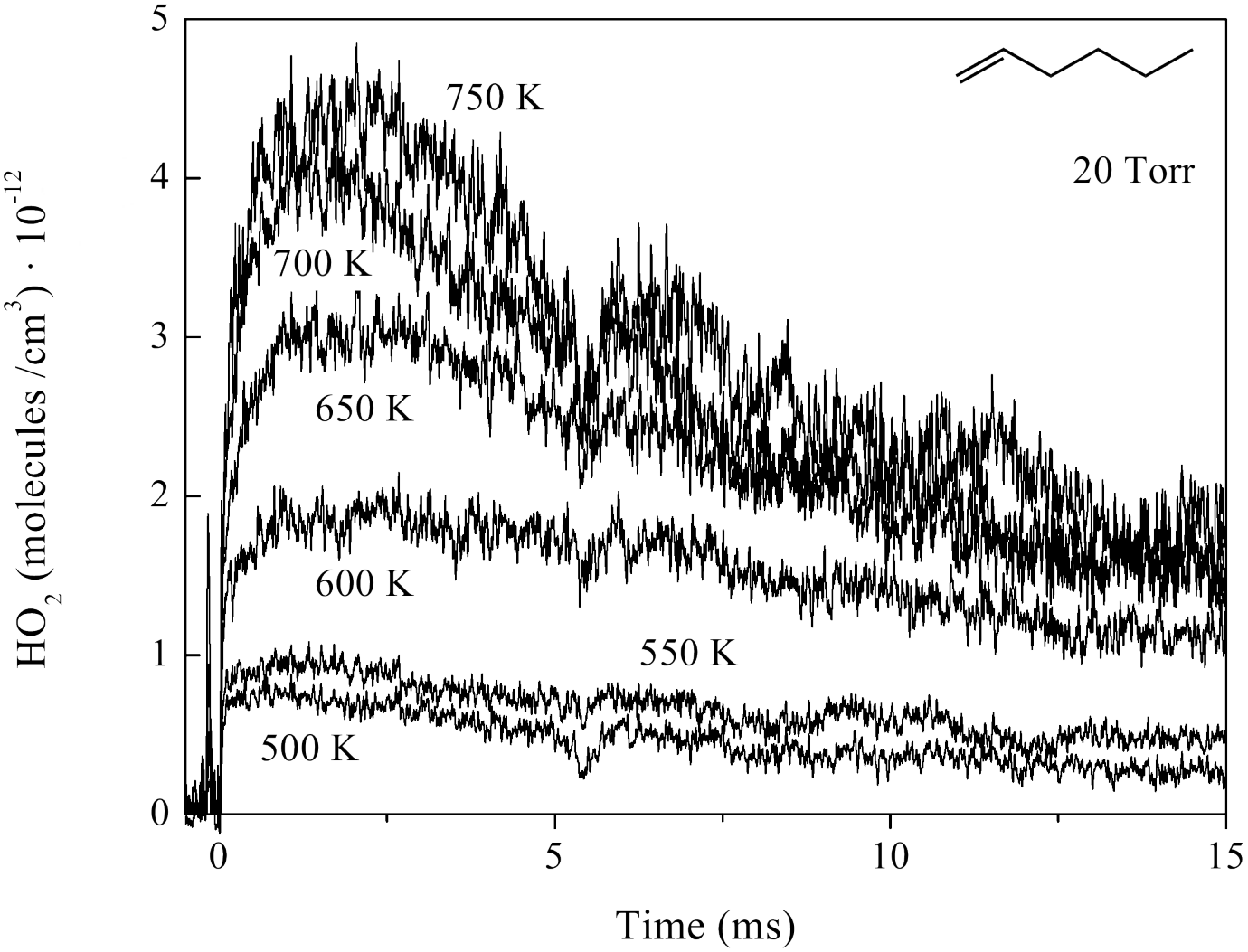


HO_2 Time History Results

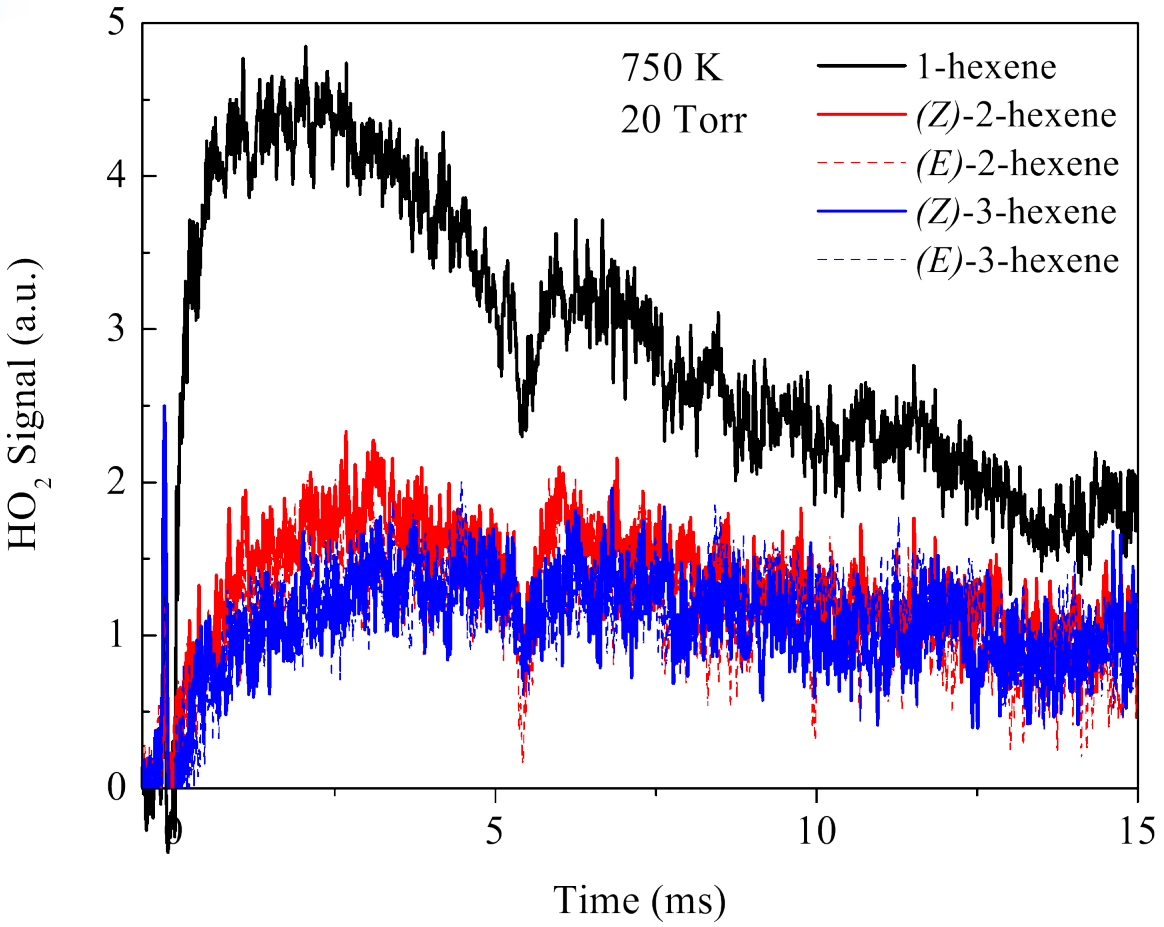
HO_2 Time Histories (1-Hexene)

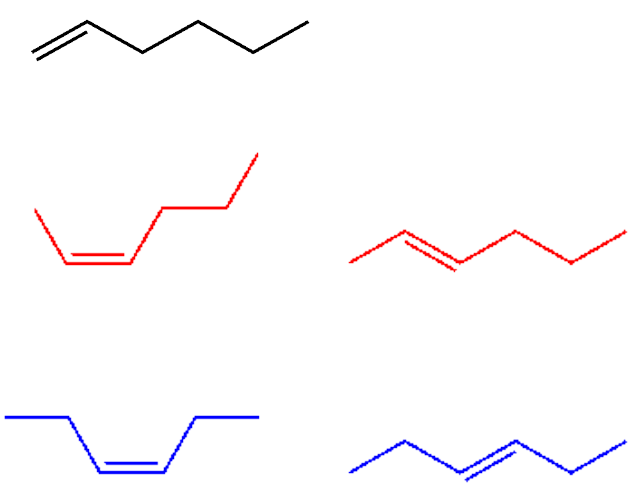


HO_2 Time Histories (1-Hexene)



HO_2 Time Histories for 1-/2-/3-Hexene Conformers (750 K)

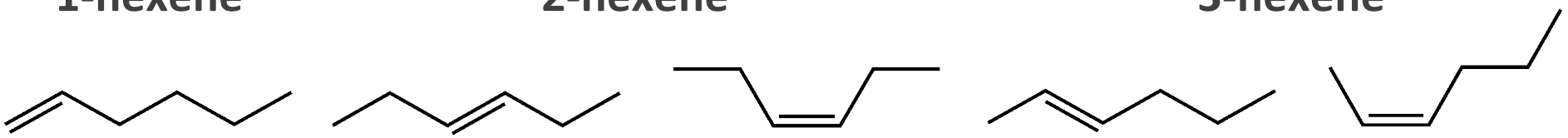




Summary of OH and HO_2 Time Histories (20 Torr)

- Temperature dependence of OH formation in hexene isomers
  - 1-hexene resembles alkane oxidation
  - 2-hexene exhibits plateauing trend
  - 3-hexene yields limited OH, peak at 550 K
  - Conformer-independent
- Temperature dependence of HO_2 formation in hexene isomers
  - HO_2 yield for 2-/3-hexene below detection limit (ca. 10^{10} cm^{-3}) below 600 K
  - Conformer-independent

1-hexene **2-hexene** **3-hexene**



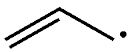
(E) *(Z)* *(E)* *(Z)*

Photoionization Mass Spectrometry Results

Difference Mass Spectra from 1-Hexene Oxidation (550 K)

conjugate alkenes (dienes)

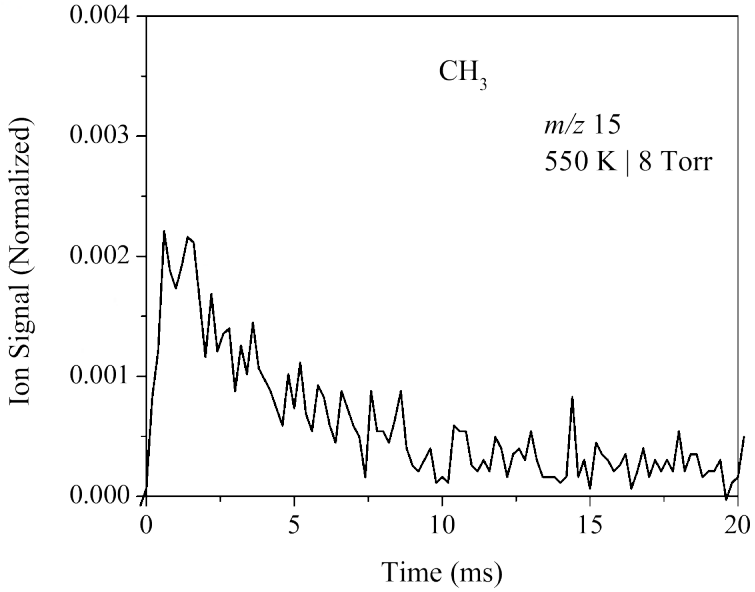
cyclic ethers

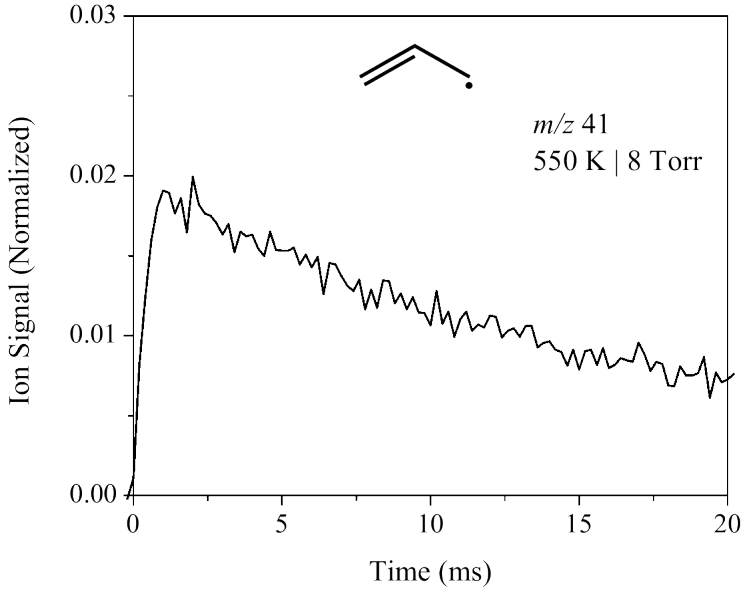


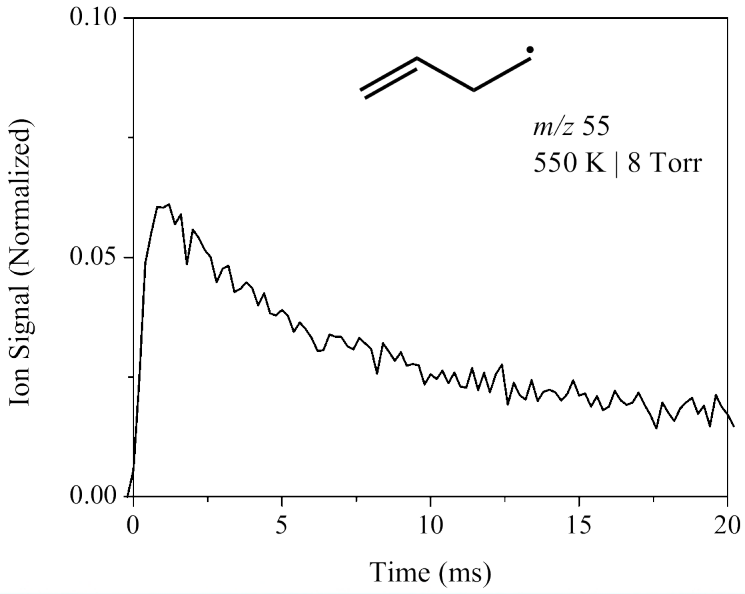
aldehydes

methyl

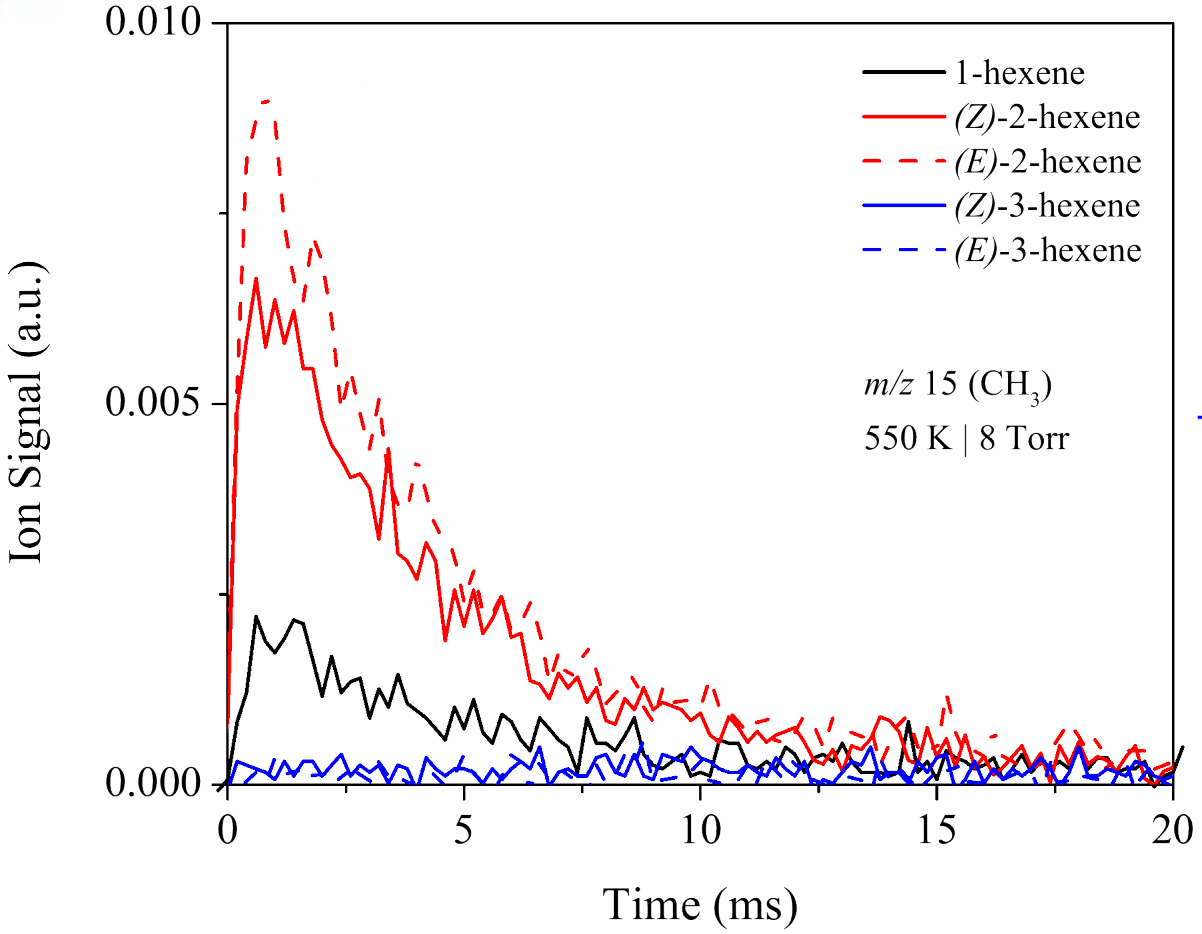
Hydrocarbon Radical Profiles in 1-Hexene Oxidation (550 K)

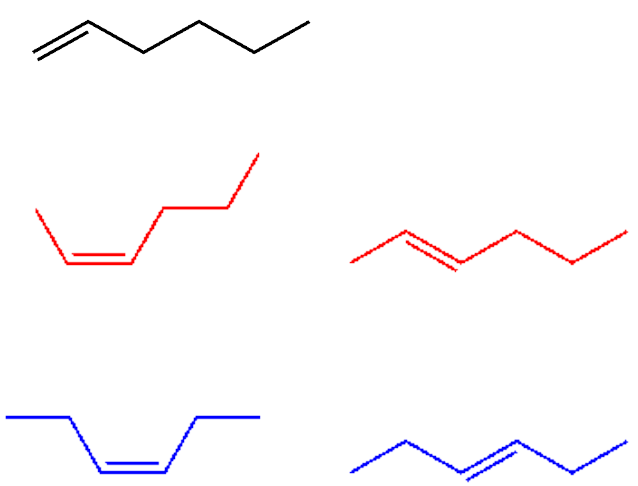




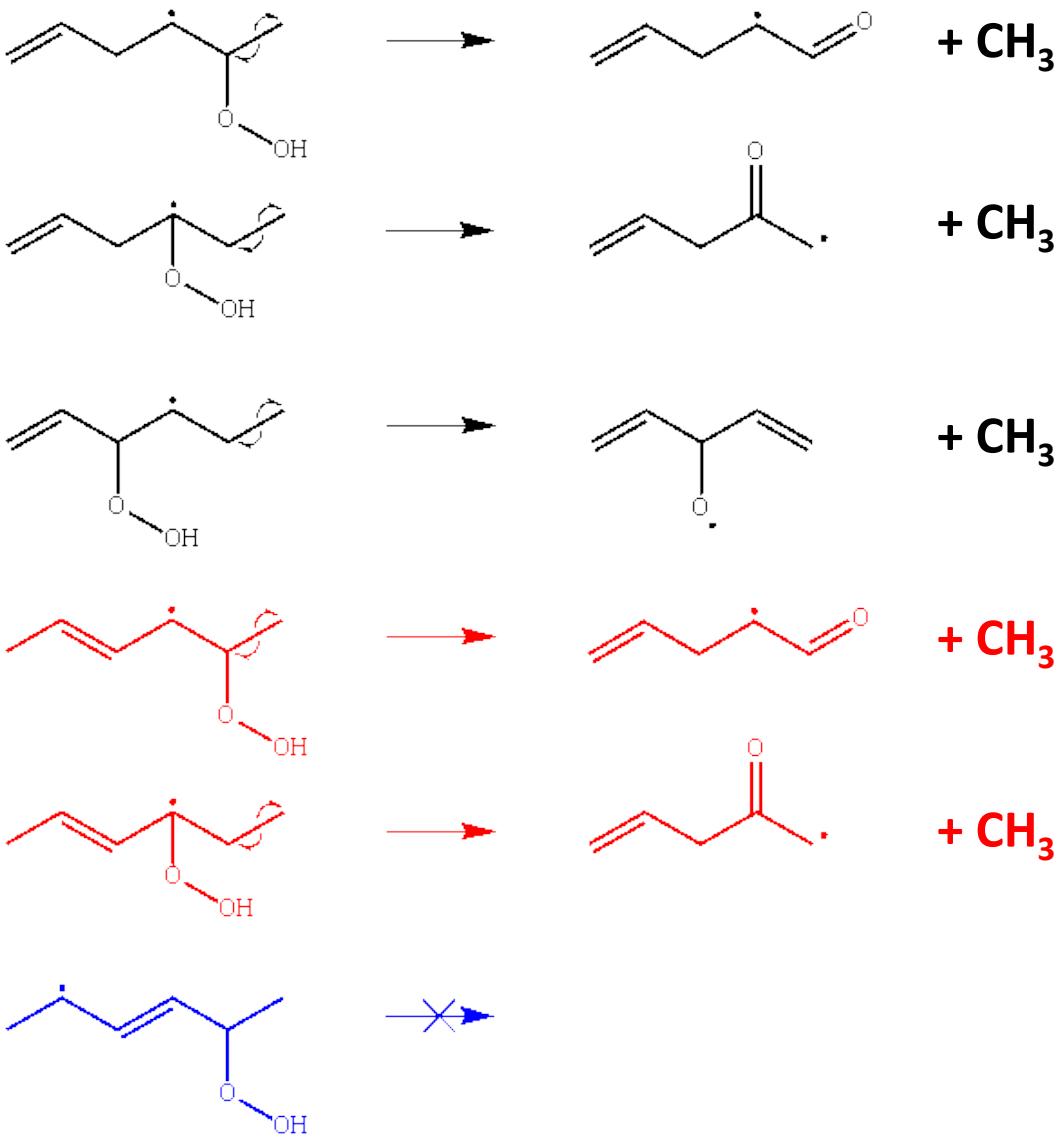


Methyl Radical Time Profiles for 1-/2-/3-Hexene (550 K) Exhibit Isomer Dependence





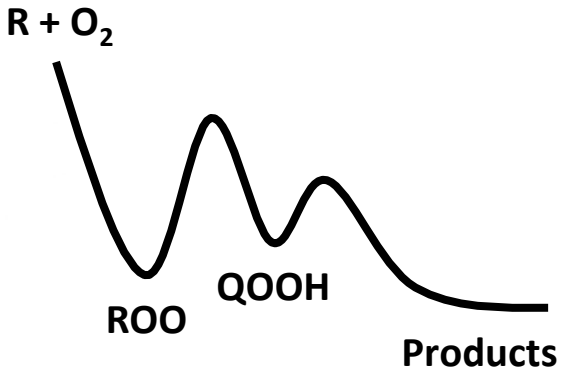
Methyl Radical Formation Pathways



Concluding Remarks on Role of C=C Bond Position in Low -Temperature Oxidation of Hexene Isomers

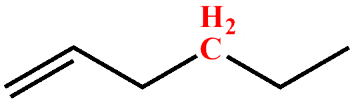
- C=C located towards the center of the molecule leads to
  - Diminished OH yield
  - Diminished HO_2 yield
- Experimental results → no *(E)/(Z)* conformer dependence
- Photoionization mass spectrometry results → evidence of co-product pairs consistent with C–C β-scission of QOOH radicals

Concluding Remarks on Role of C=C Bond Position in Low -Temperature Oxidation of Hexene Isomers



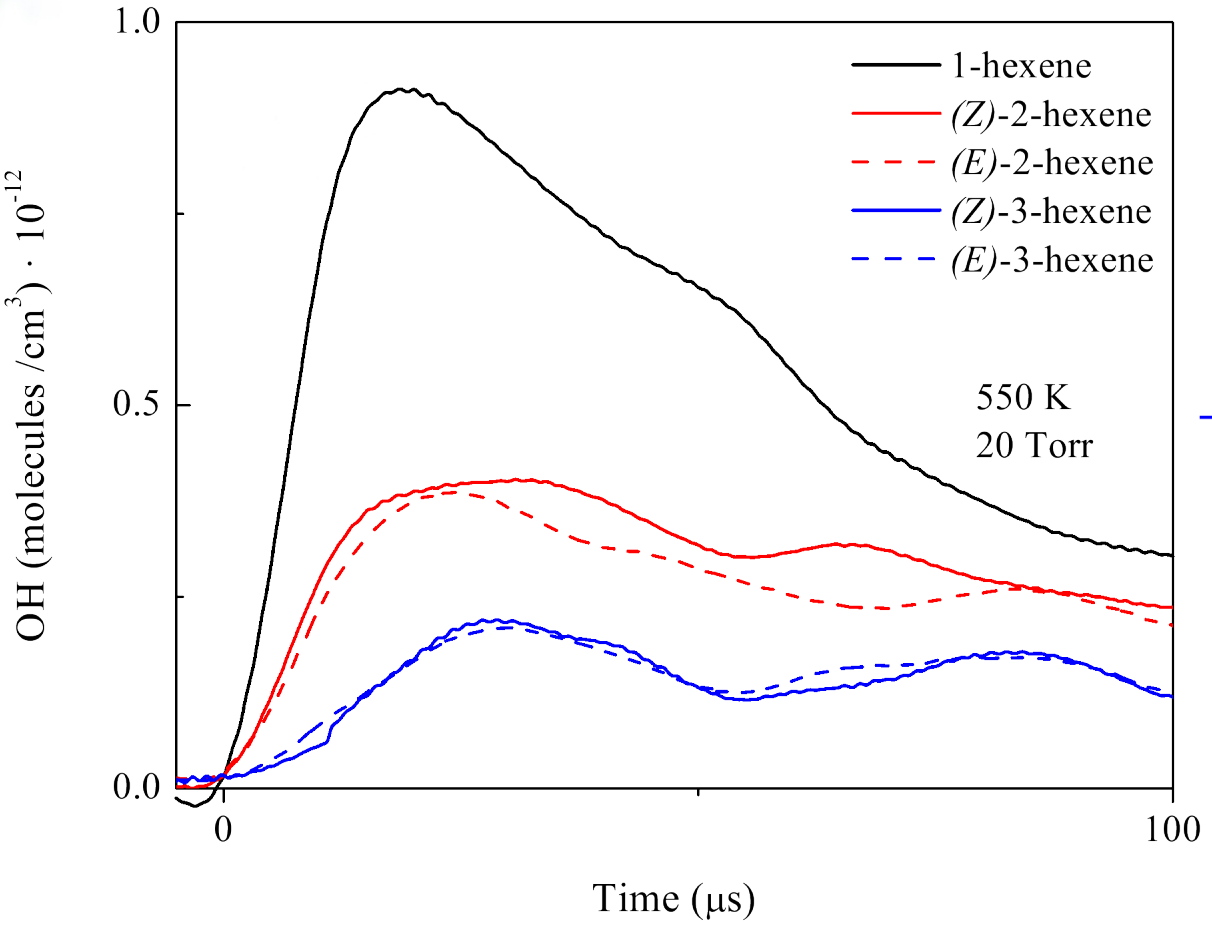
- Potential energy surface calculations for hexenyl + O_2
  - Effect of allylic stabilization on C–C bond scission in QOOH
- Master Equation calculations of select reaction rates

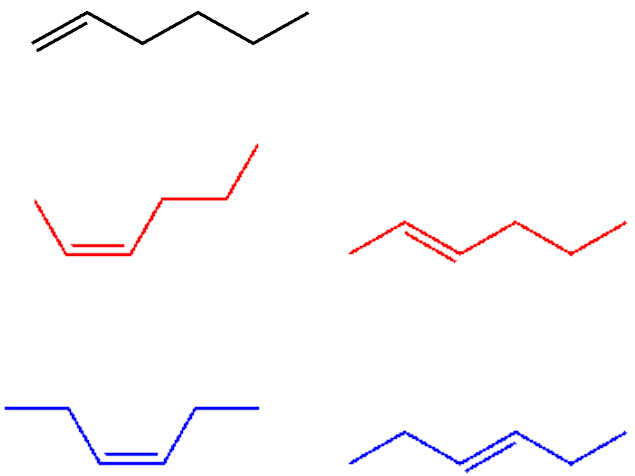
Radical Distribution from RH + Cl → R + HCl using SAR: 1-Hexene



$$k(T) = k_p(T)F(-CH_2-) + k_s(T)F(-CH_2-)F(-CH_3) + k_s(T)F(-CH_2-)F(allylic) + k_{s,a}(T)F(=CH_2-)F(-CH_2-)$$

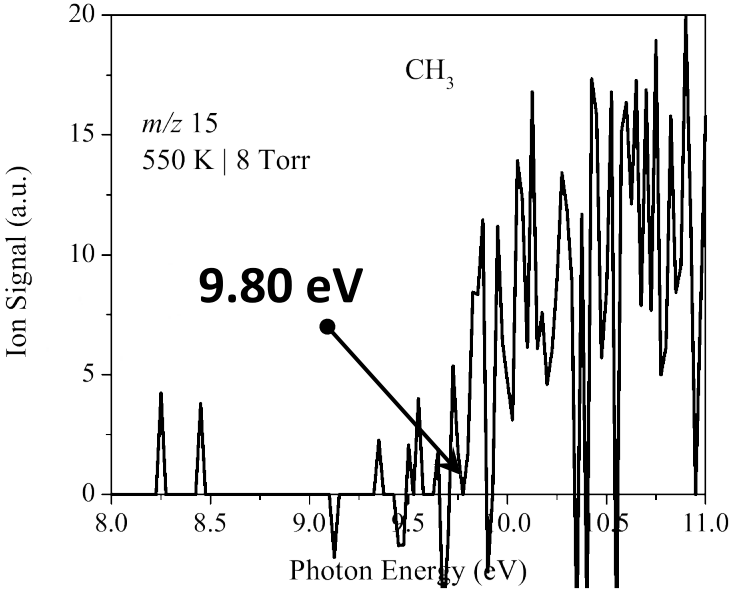
OH Time Profiles of Hexene Isomers/Conformers (550 K)

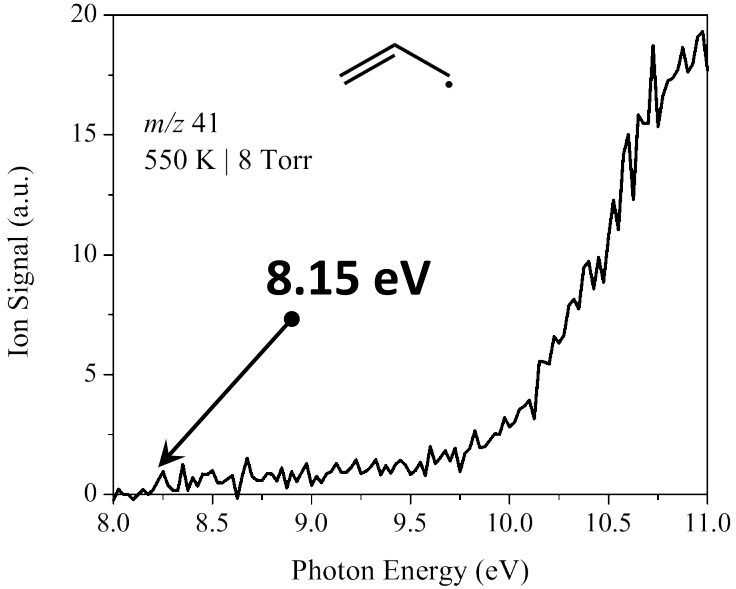


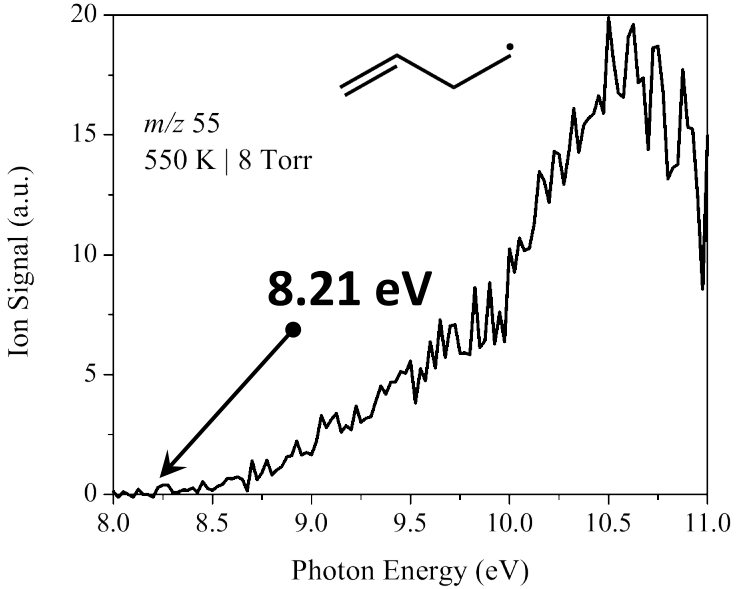


Photoionization Spectra from 1-Hexene Oxidation (550 K)

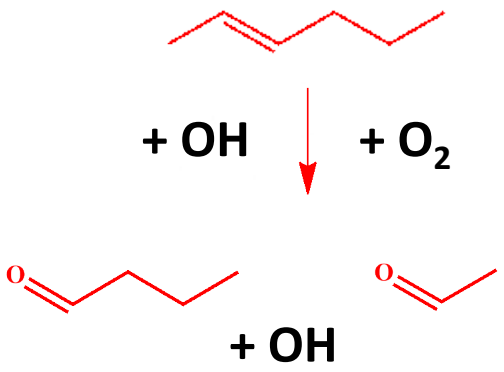
Photoionization Spectra from 1-Hexene Oxidation (550 K)

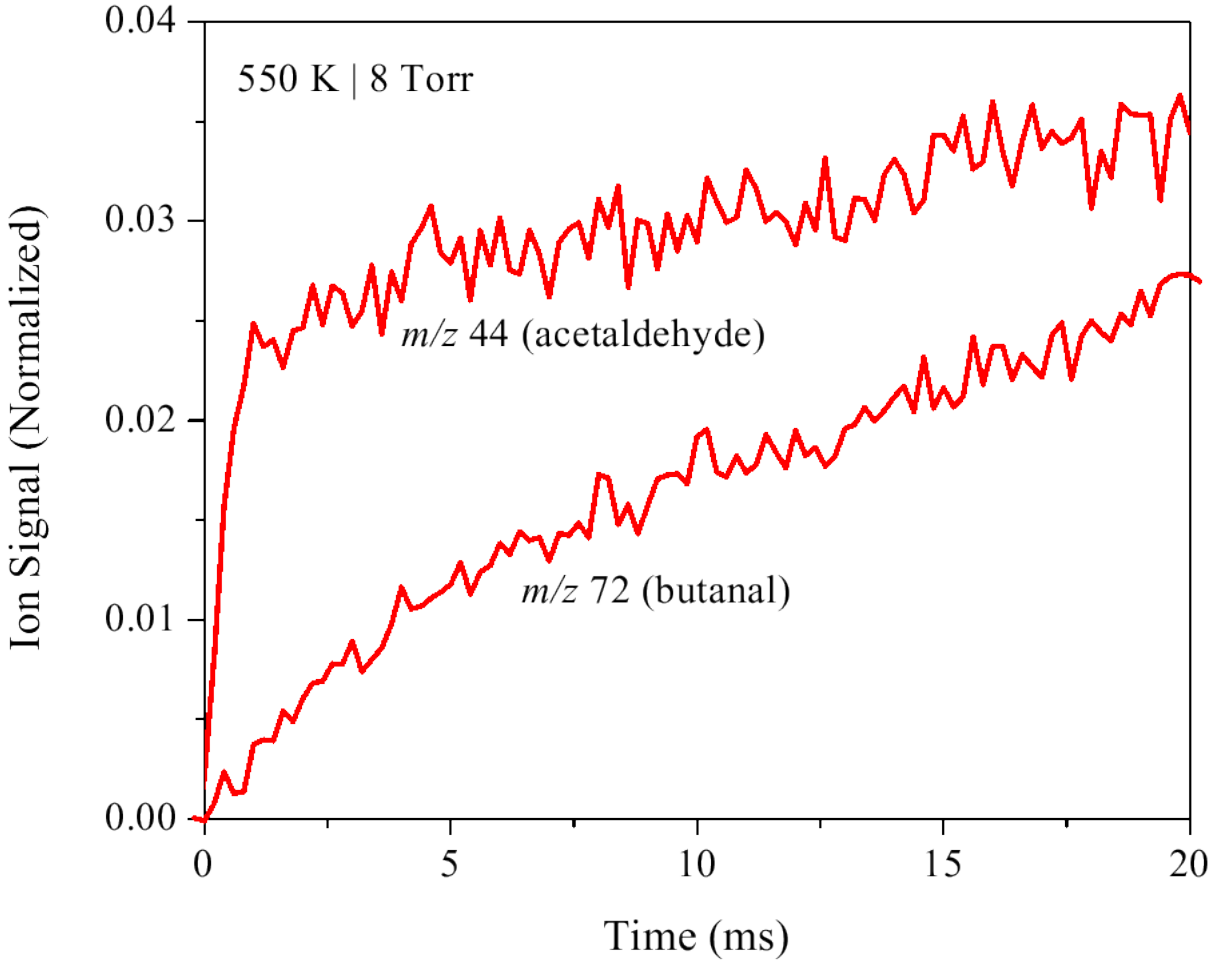




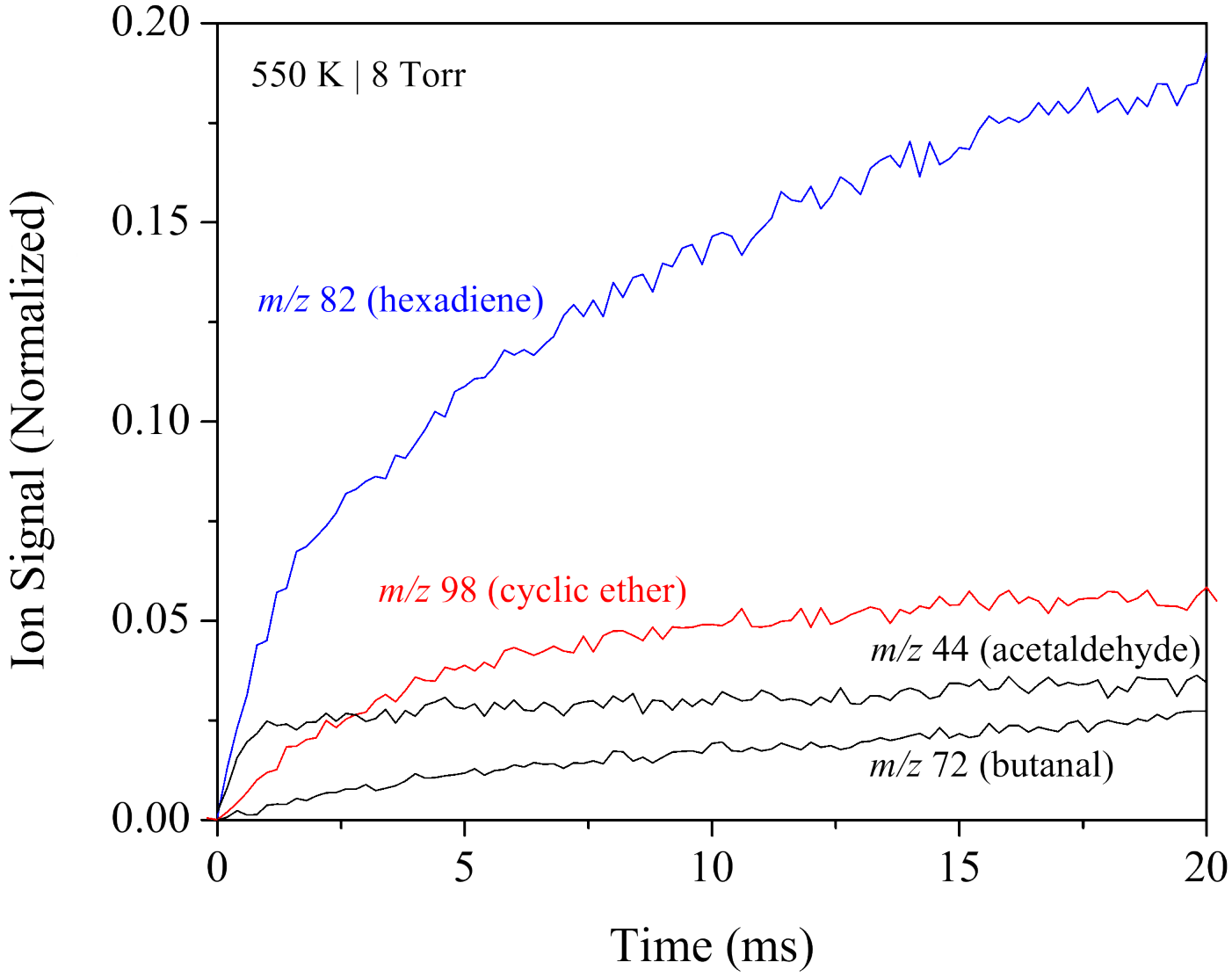


Product Formation from the Waddington Mechanism in *(Z)*-2-hexene Oxidation (550 K)

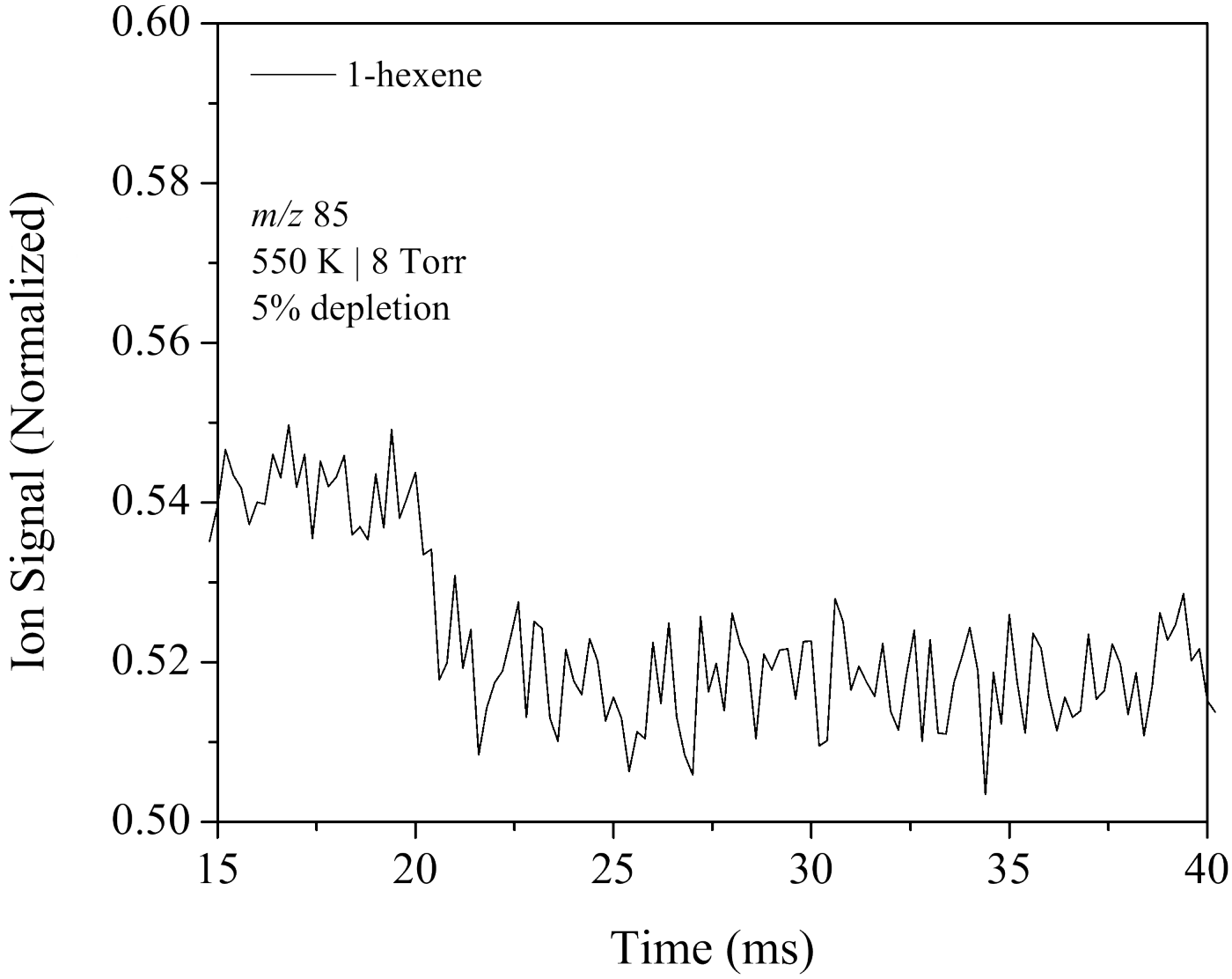




Comparison of Cyclic Ether, Conjugate Alkene Time Histories to Products of C–C β-Scission QOOH and Waddington



Fuel-Depletion Percentages of 5% (MPIMS)

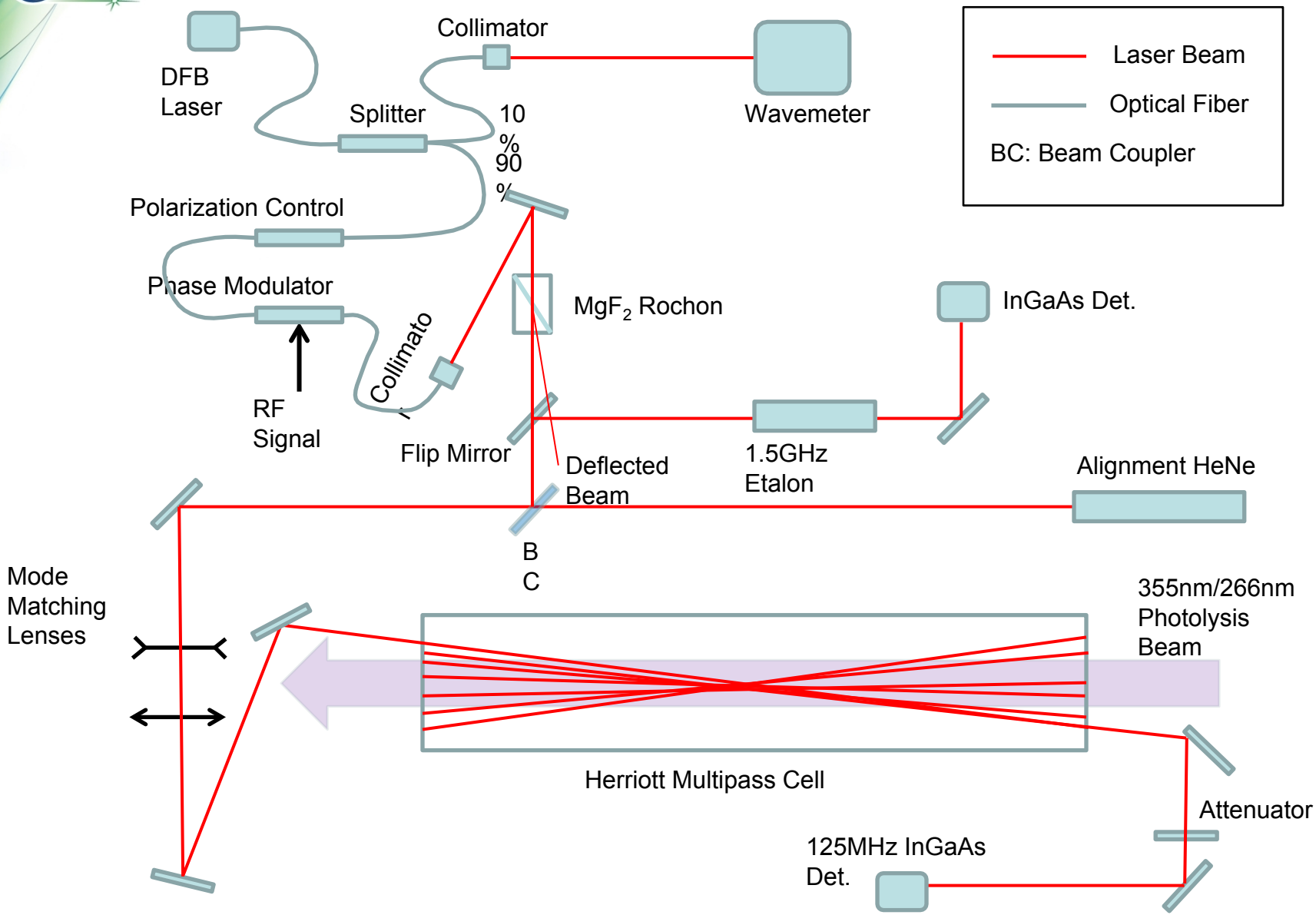


Rate Parameters of Other OH Depletion Reactions

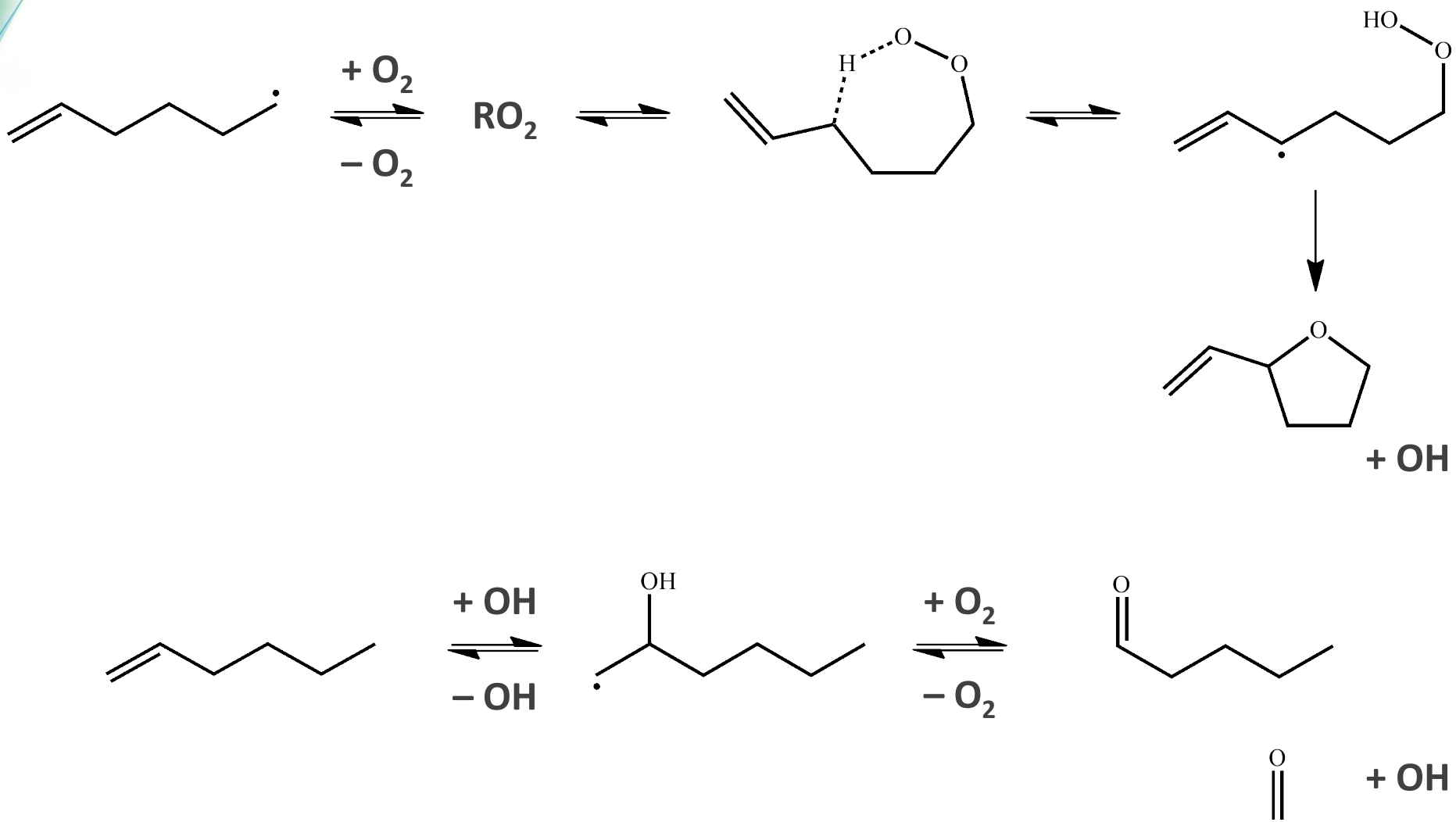
reaction	□□	□□	□□□ / kcal mol^{-1}	□□(600 □□) / cm^3 molec.$^{-1}$ s^{-1}	reference
OH + 1-hexene → products*	–	–	–	$1.83 \cdot 10^{-11}$	[24]
OH + 2-hexene → products*	–	–	–	$1.35 \cdot 10^{-11}$	[24]
OH + 3-hexene → products*	–	–	–	$8.76 \cdot 10^{-12}$	[24]
OH + OH → H_2O + O	$1.83 \cdot 10^{-19}$	2.11	2.9	$7.03 \cdot 10^{-20}$	[24]
OH + OH → H_2O + H	$2.70 \cdot 10^{-13}$	0.00	–0.9	$5.75 \cdot 10^{-13}$	[25]
M + OH + OH → M + H_2O_2	$6.07 \cdot 10^{-16}$	1.14	–2.6	$1.18 \cdot 10^{-14}$ **	[24]
OH + OH → HO_2 + H	$3.37 \cdot 10^{-14}$	0.72	36.8	$2.15 \cdot 10^{-27}$	[24]
OH + OH → H_2 + O_2	$3.32 \cdot 10^{-12}$	0.51	50.4	$2.02 \cdot 10^{-30}$	[26]

** Rate in the high-pressure limit

Two-Tone Frequency Modulation Schematic



Select OH Formation Mechanisms (1-hexene)

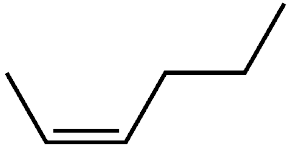


Hexene Isomers Permit Detailed Study on the Influence of C=C Position on Low-Temperature Autoignition Chemistry

1-hexene 

2-hexene 

(E)-2-hexene

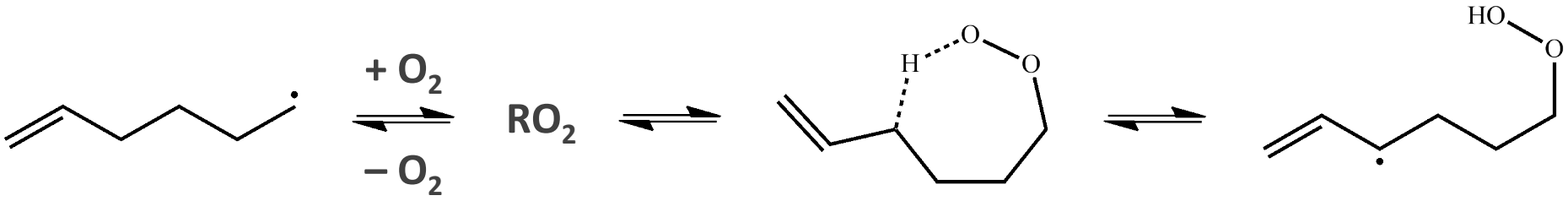


(Z)-2-hexene

3-hexene 

(E)-3-hexene

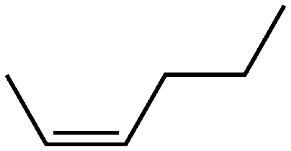
(Z)-3-hexene



C=C Position Affects Distribution of Allylic, 1°, 2° C–H Bonds

1-hexene 

2-hexene 

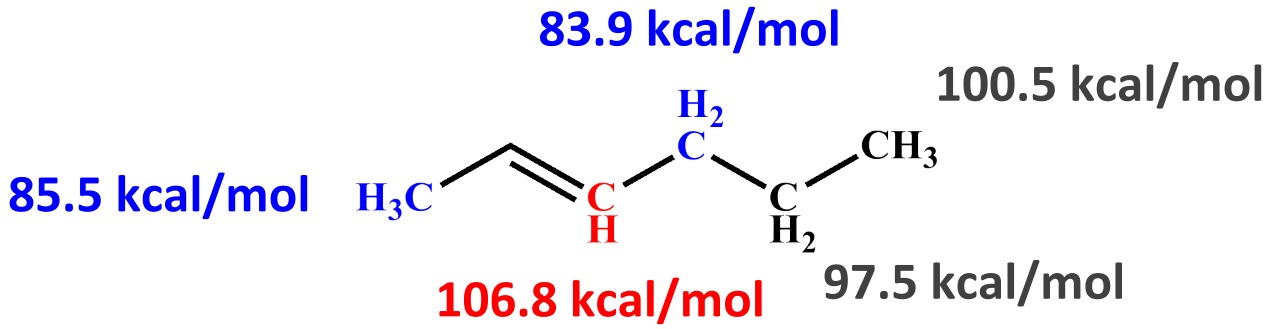
(E)-2-hexene 

(Z)-2-hexene

3-hexene 

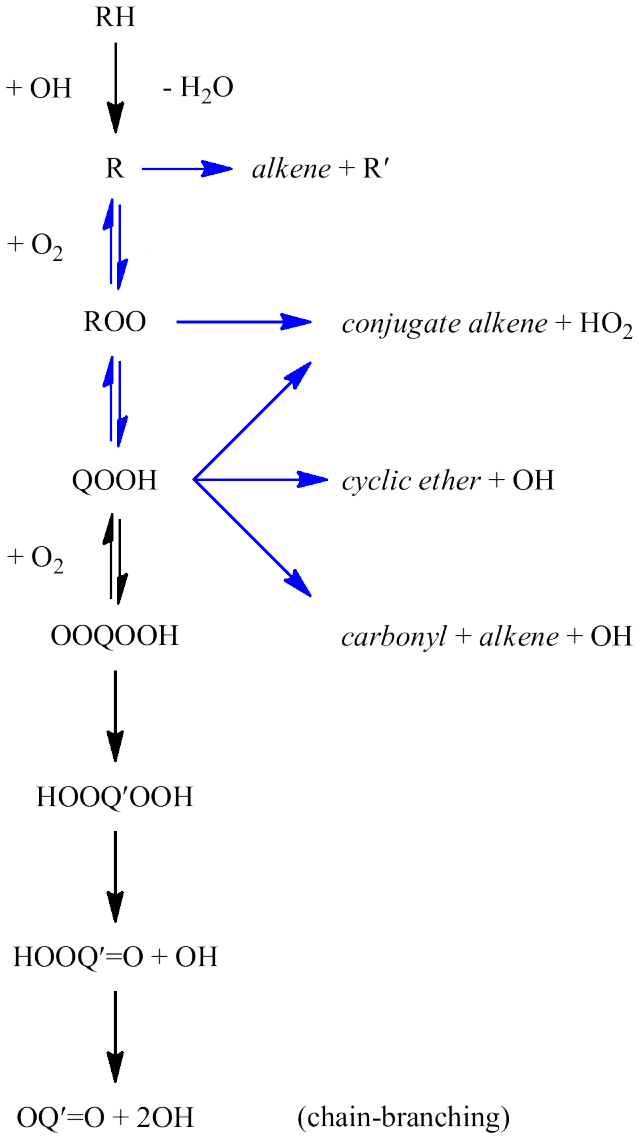
(E)-3-hexene 

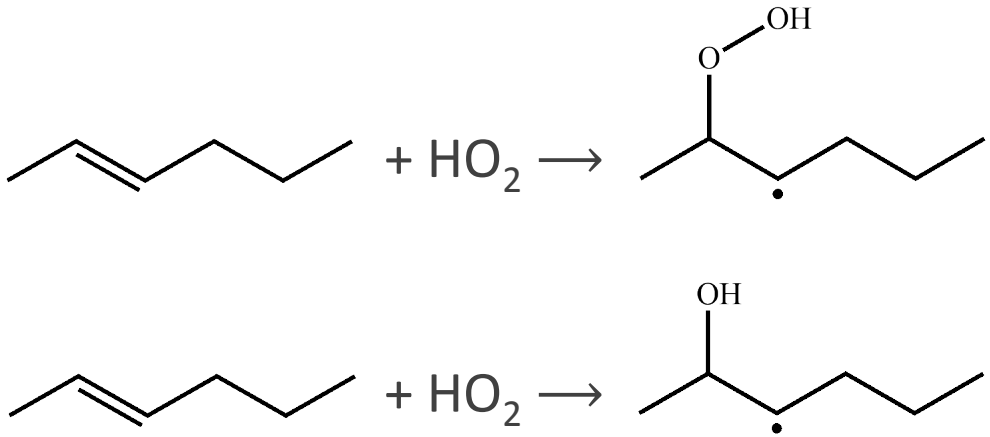
(Z)-3-hexene



(E)-2-hexene C–H bond dissociation energies

Alkene Oxidation Requires Additional Reaction Sequences Compared to Alkane Oxidation



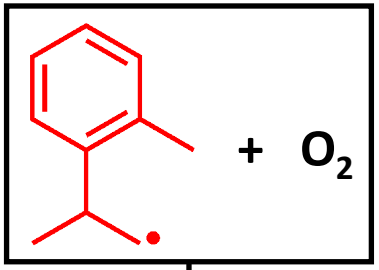


$R + O_2 \longrightarrow QOOH \longrightarrow vinyloxy + C_4H_8O$

Experimental Approach – Studying R + O_2 Chemistry using Multiplexed Photoionization Mass Spectrometry (MPIMS)

+ He

Photolysis



+ O_2 + Cl_2 + He

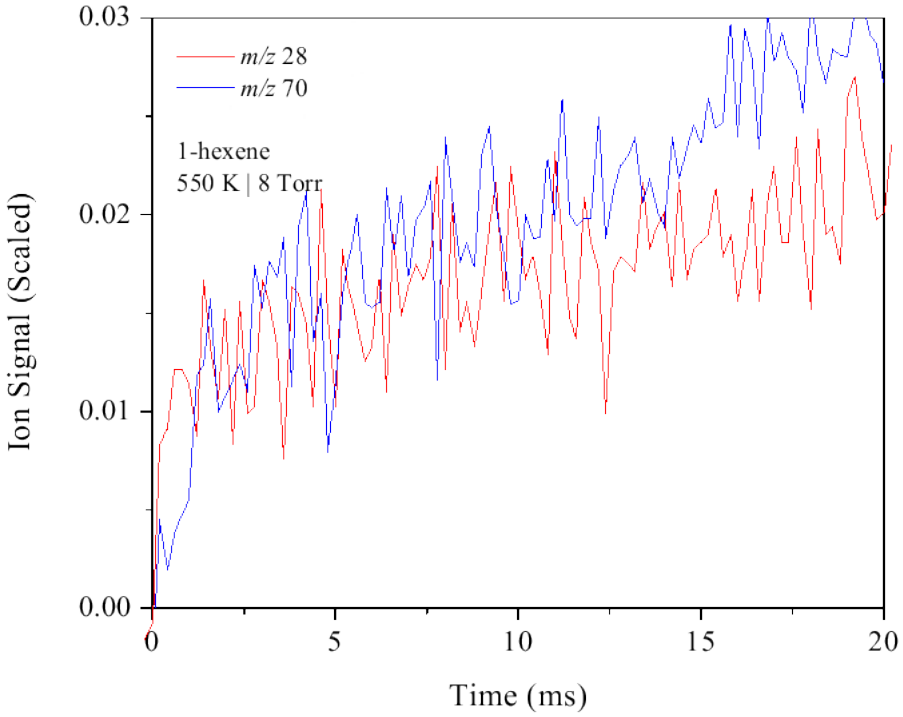
System of Interest (R + O_2)

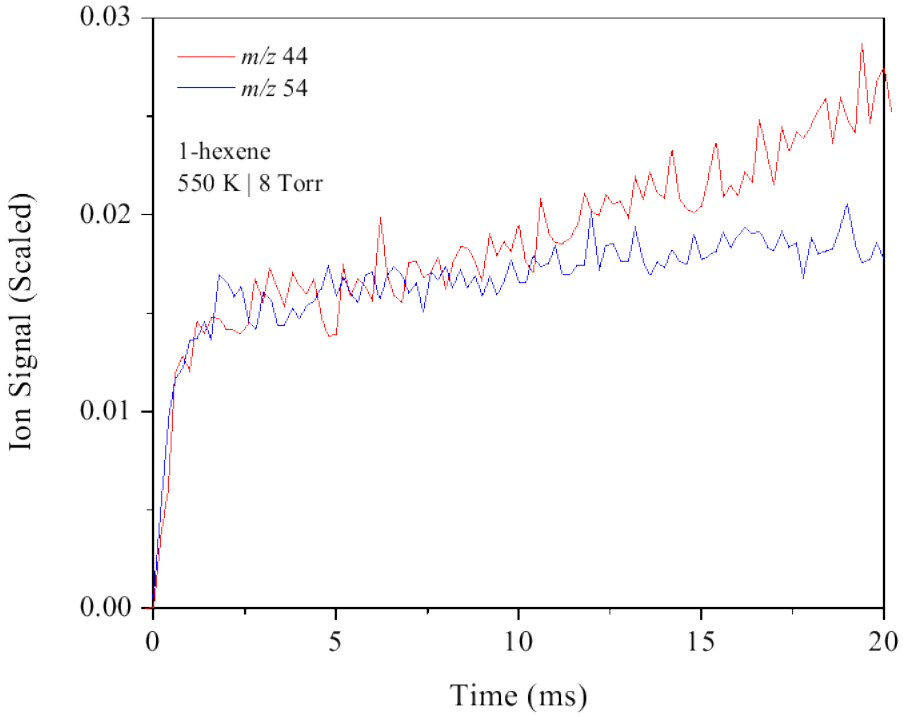
Multiplexed Photoionization Mass Spectrometer

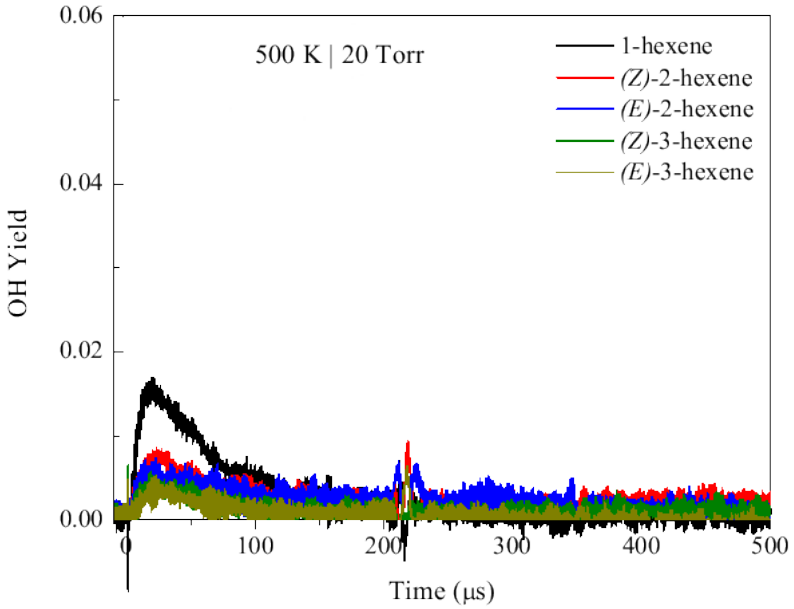
450 – 700 K

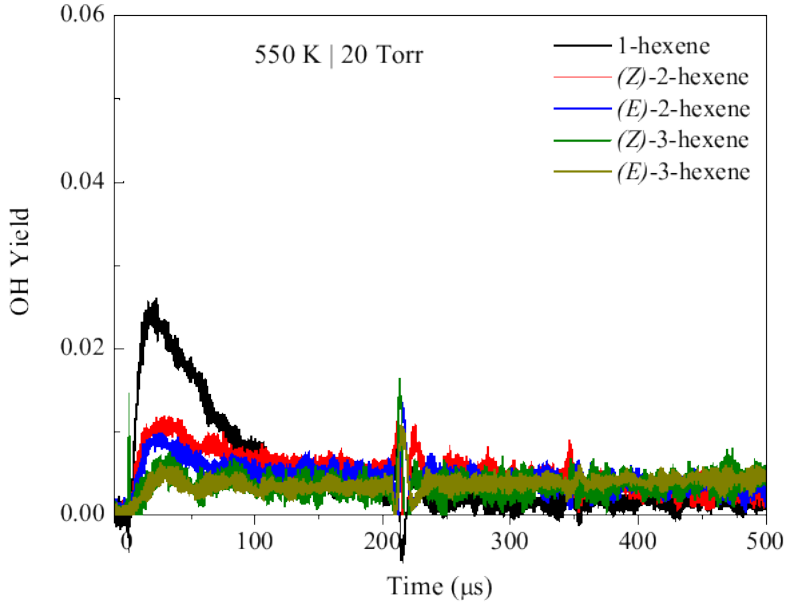
8 Torr

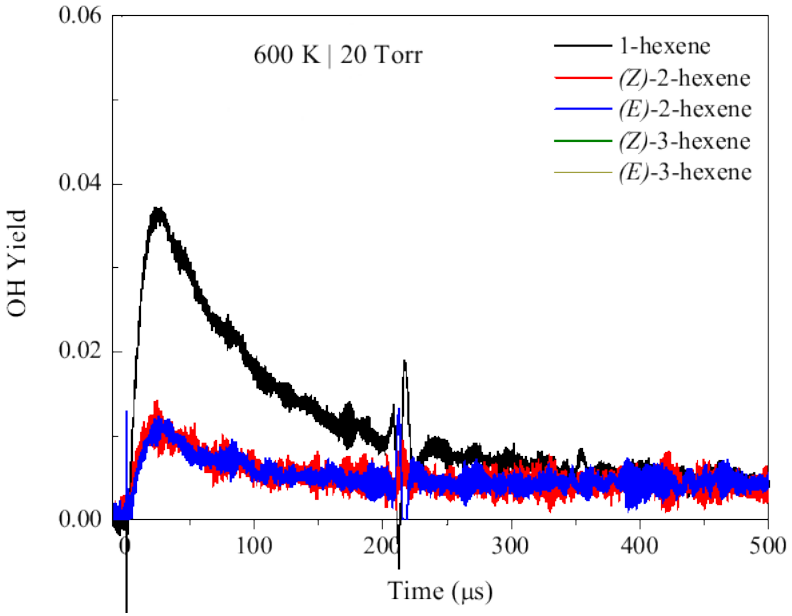
Osborn et al., *Rev. Sci. Inst.* (2008)

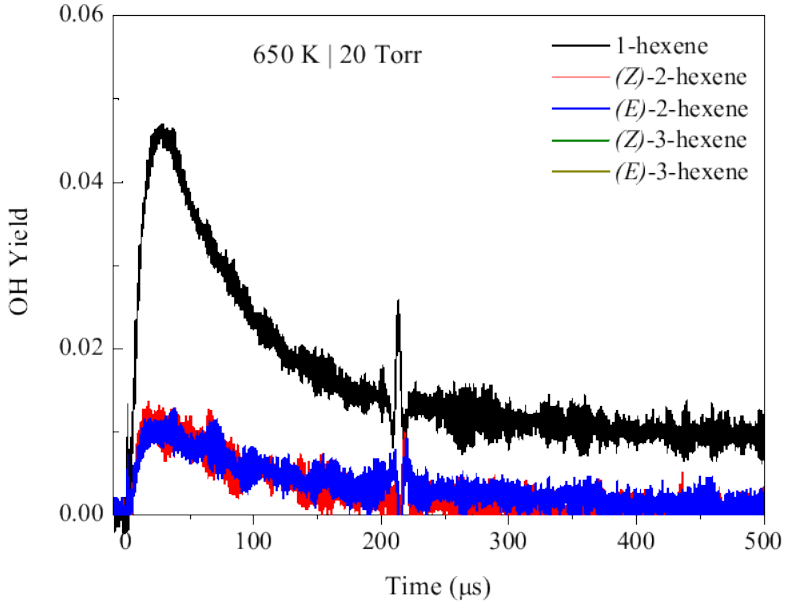

0.03
0.02
0.01
0.00
Ion Signal (Scaled)
m/z 28
m/z 70
1-hexene
550 K | 8 Torr
0
5
10
15
20
Time (ms)

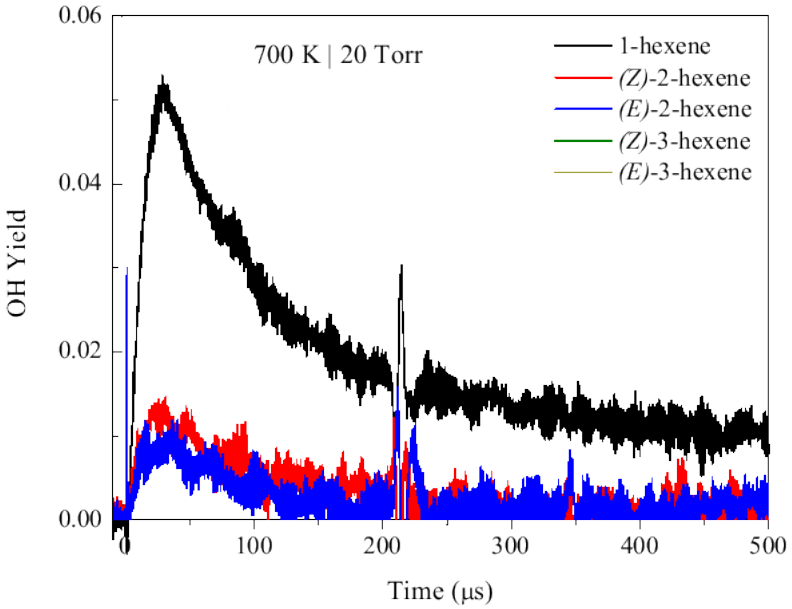

0.03
0.02
0.01
0.00
Ion Signal (Scaled)
m/z 44
m/z 54
1-hexene
550 K | 8 Torr
0
5
10
15
20
Time (ms)

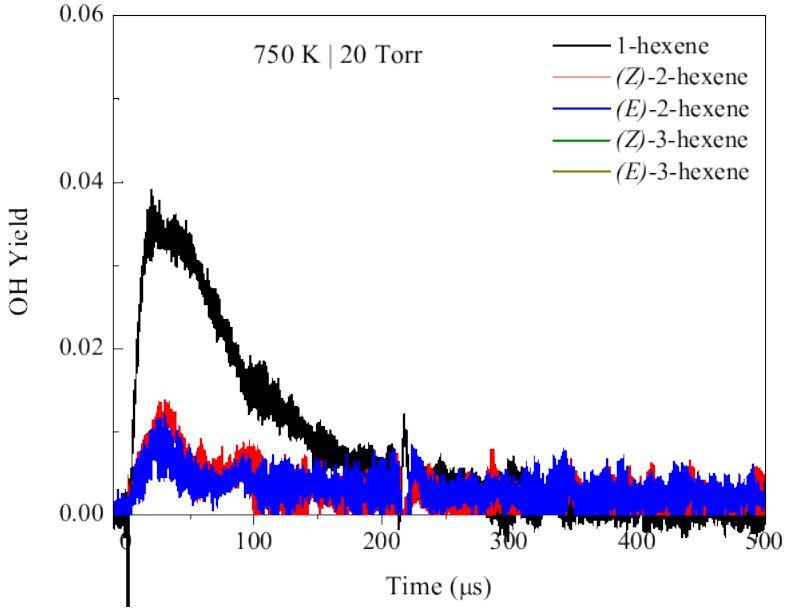

500 K | 20 Torr
1-hexene
(Z)-2-hexene
(E)-2-hexene
(Z)-3-hexene
(E)-3-hexene
OH Yield
0.06
0.04
0.02
0.00
0
100
200
300
400
500
Time (μs)


550 K | 20 Torr
1-hexene
(Z)-2-hexene
(E)-2-hexene
(Z)-3-hexene
(E)-3-hexene
OH Yield
0.06
0.04
0.02
0.00
0
100
200
300
400
500
Time (μs)


600 K | 20 Torr
1-hexene
(Z)-2-hexene
(E)-2-hexene
(Z)-3-hexene
(E)-3-hexene
OH Yield
0.06
0.04
0.02
0.00
0
100
200
300
400
500
Time (μs)


650 K | 20 Torr
1-hexene
(Z)-2-hexene
(E)-2-hexene
(Z)-3-hexene
(E)-3-hexene
OH Yield
0.06
0.04
0.02
0.00
0
100
200
300
400
500
Time (μs)


700 K | 20 Torr
1-hexene
(Z)-2-hexene
(E)-2-hexene
(Z)-3-hexene
(E)-3-hexene
OH Yield
0.06
0.04
0.02
0.00
0
100
200
300
400
500
Time (μs)


750 K | 20 Torr
1-hexene
(Z)-2-hexene
(E)-2-hexene
(Z)-3-hexene
(E)-3-hexene
OH Yield
0.06
0.04
0.02
0.00
0
100
200
300
400
500
Time (μs)

Literature on Hexene Oxidation/Autoignition

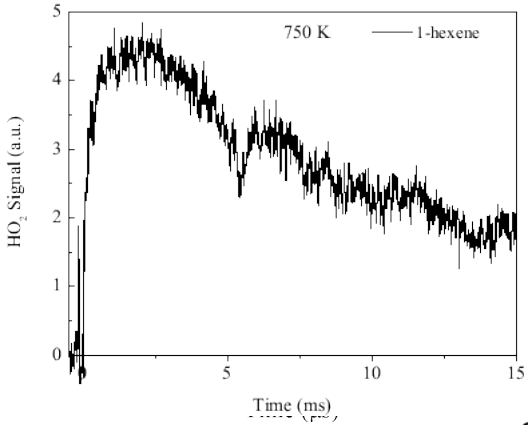
isomer	T (K)	P (atm)	%RH	ϕ	apparatus
1-/2-/3-hexene	630 – 850	8	2.3	1	RCM [9]
1-/2-/3-hexene	500 – 1100	1	1.0, 2.0	1	JSR [12]
1-/2-/3-hexene	990 – 1770	10	2.3	1	shock tube [11]
1-hexene	1250 – 1700	2	0.1, 0.4	0.5, 1.0, 1.5	shock tube [15]
1-hexene	1360 – 1780	10	0.1	0.5, 1.0, 2.0	shock tube [5]
1-hexene	750 – 1200	10	0.1	0.5, 1.0, 2.0	JSR [5]

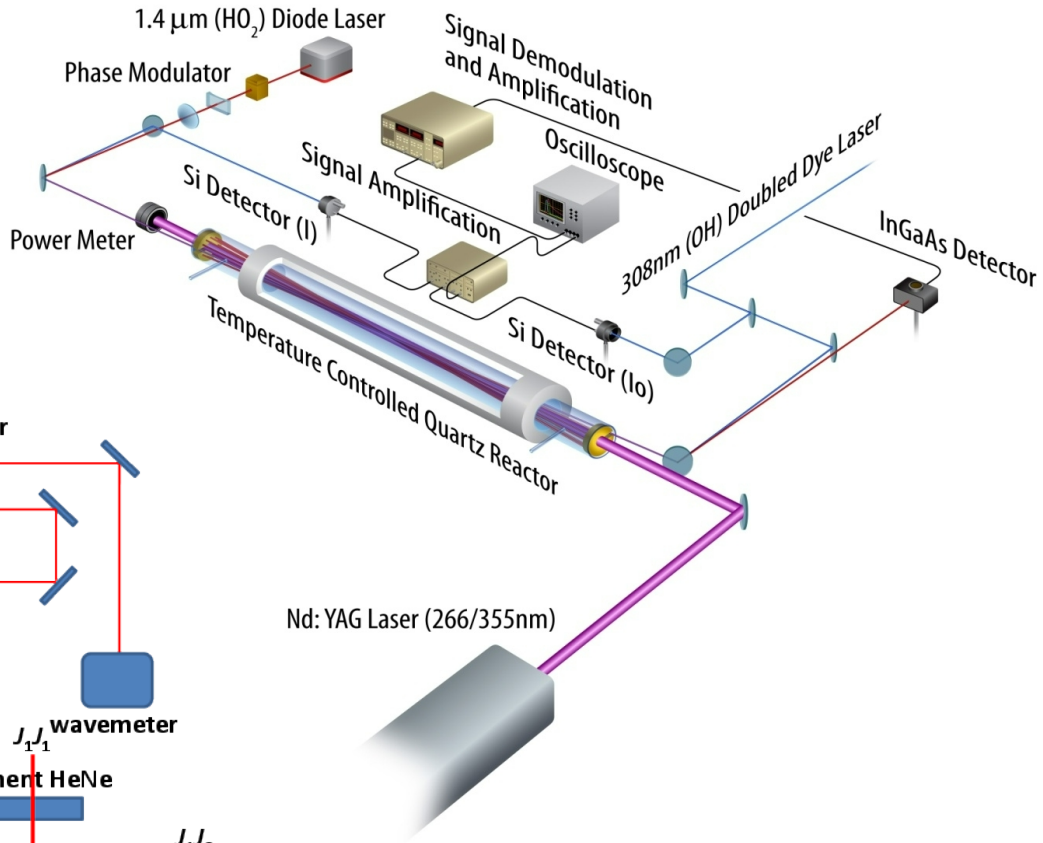
- 1-/2-hexene display two-stage ignition behavior, 3-hexene ⟶ negligible
- Two comprehensive chemical kinetics models for combustion
  - Mehl et al. (LLNL/POLIMI)
  - Battin-Leclerc (EXGAS)

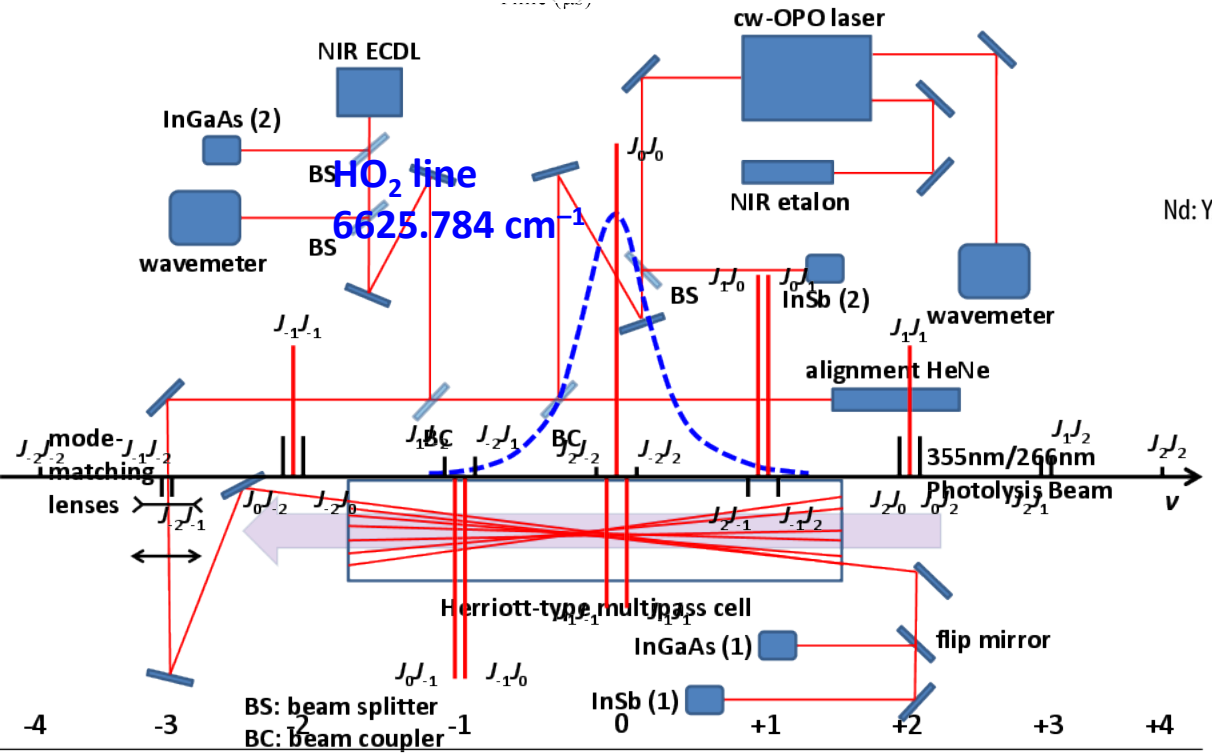
HO_2 Time Histories Corrected for HO_2 + HO_2 Self-Reaction

Upper Limit of HO_2 Formation from Oxidation of 1-hexene, *(Z)*-2-hexene, *(E)*-2-hexene, *(Z)*-3-hexene, *(E)*-3-hexene

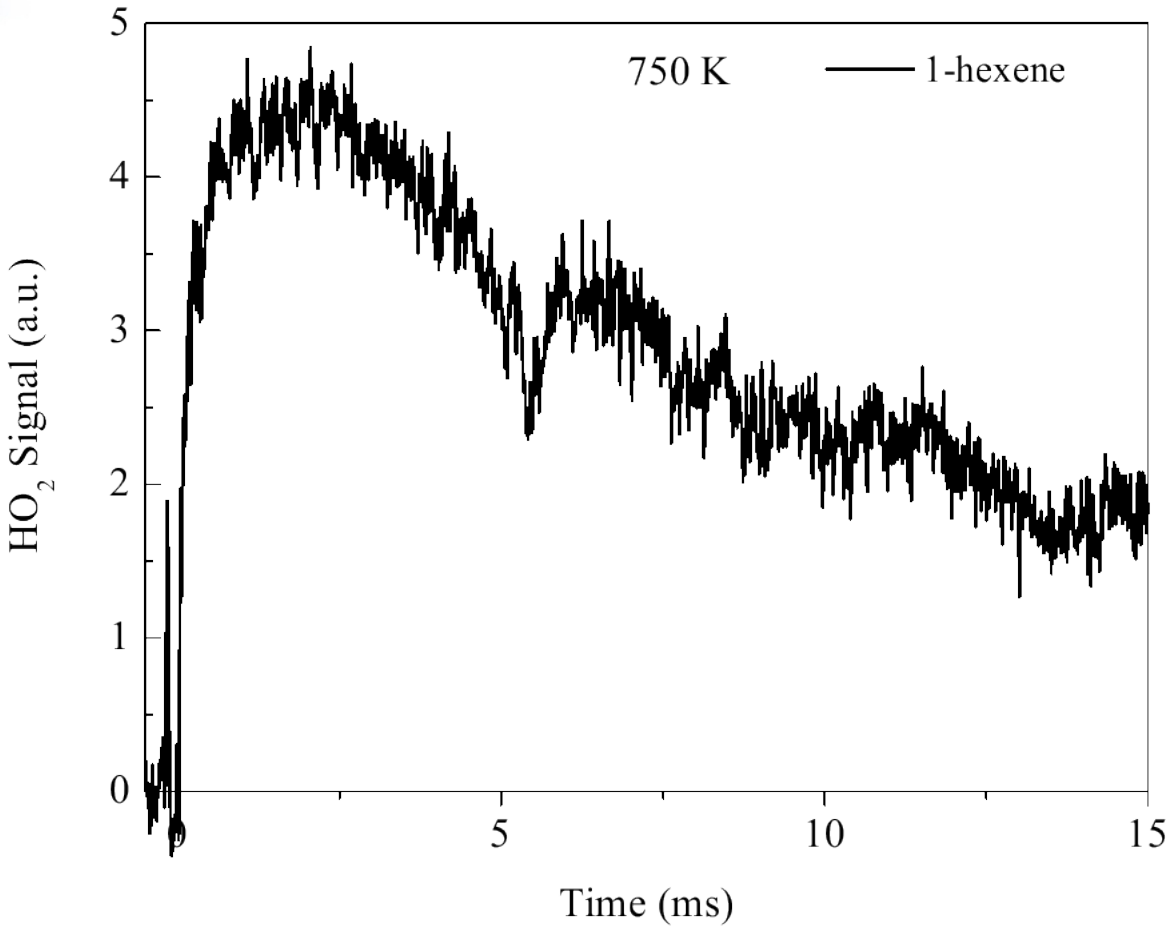
Multi-pass Infrared-Absorption Experiment



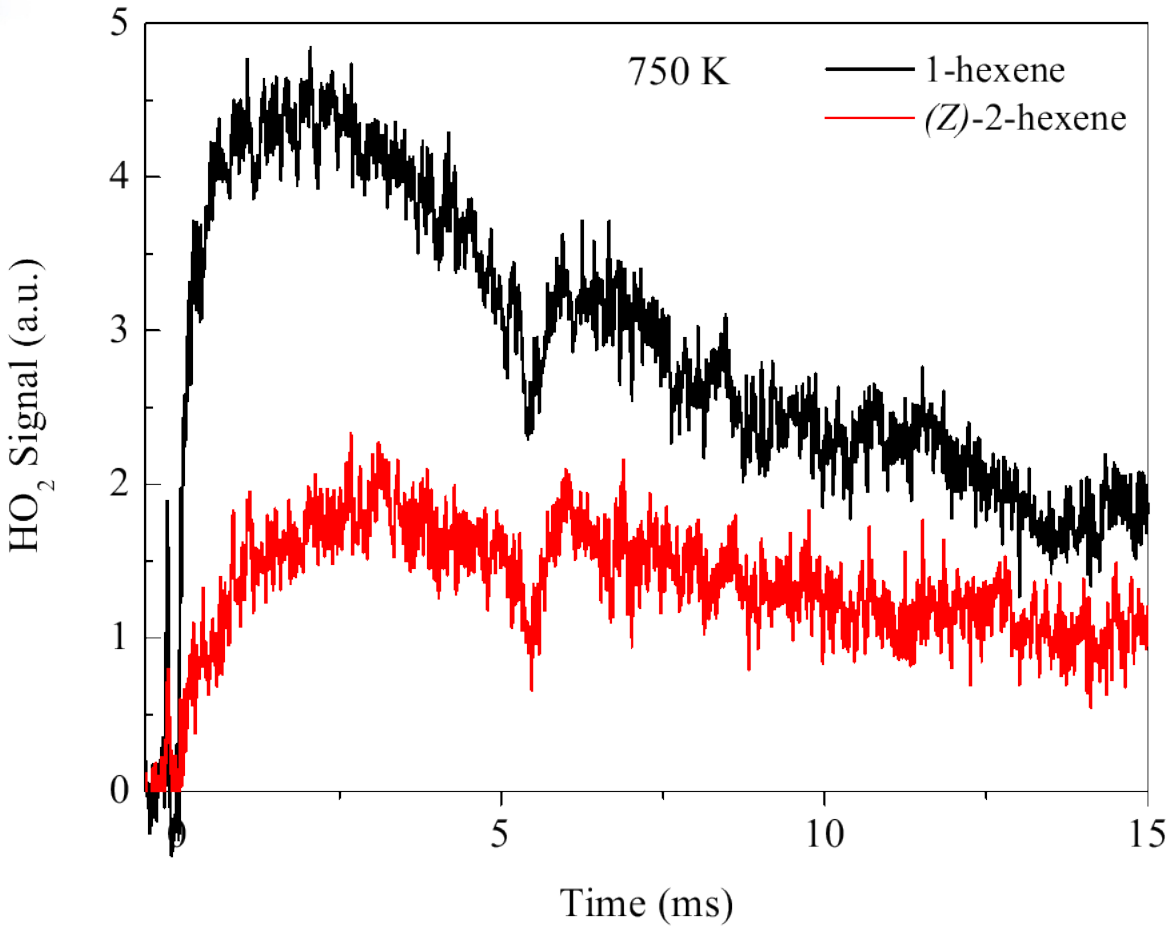


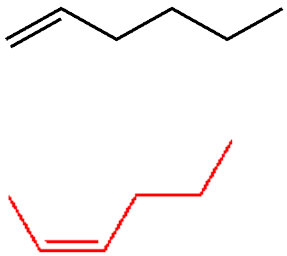


HO_2 Time Histories for 1-/2-/3-Hexene Conformers (750 K)

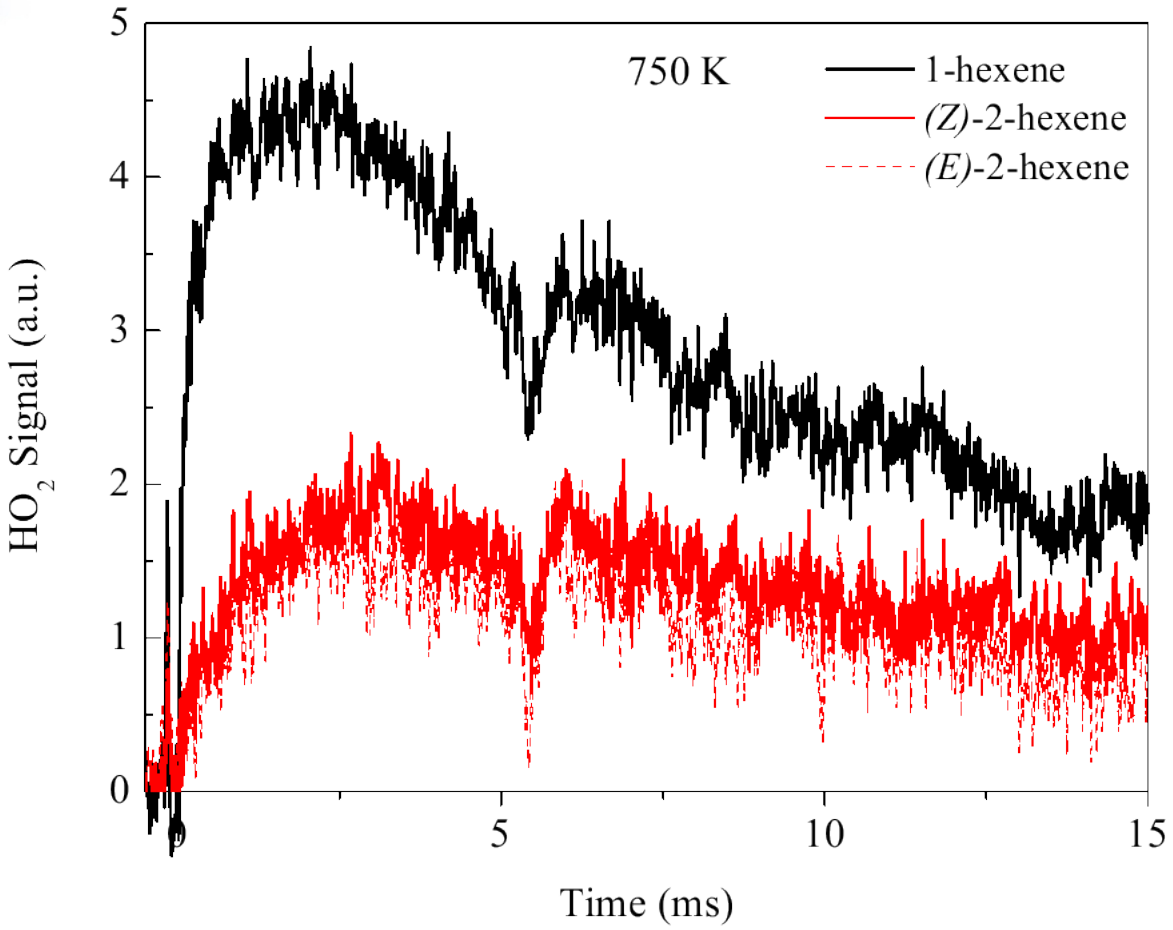


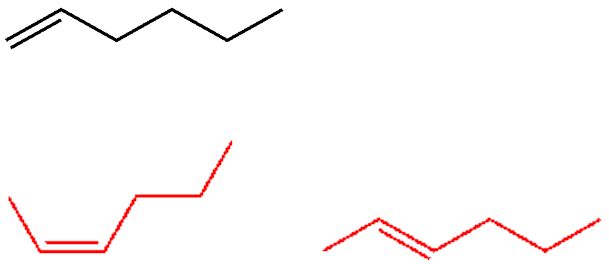
HO_2 Time Histories for 1-/2-/3-Hexene Conformers (750 K)



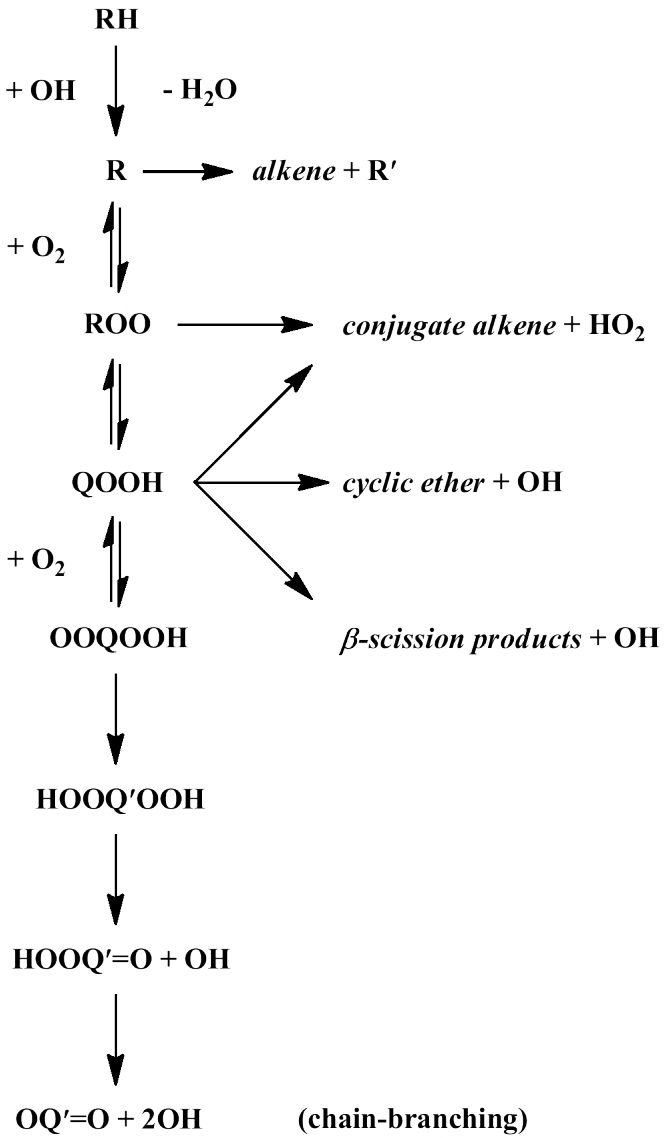


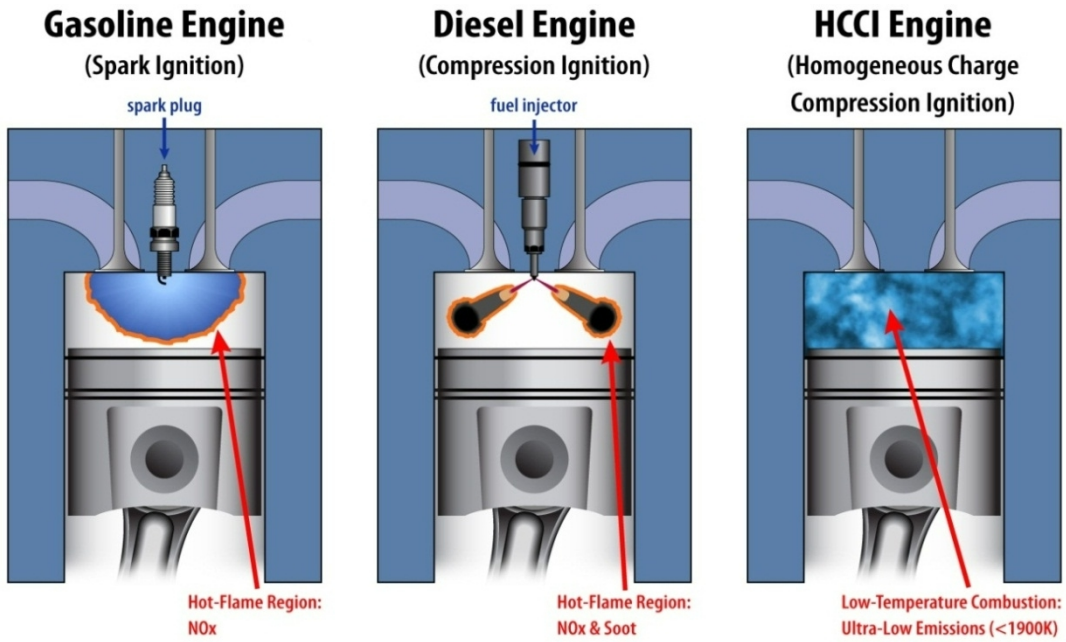
HO_2 Time Histories for 1-/2-/3-Hexene Conformers (750 K)



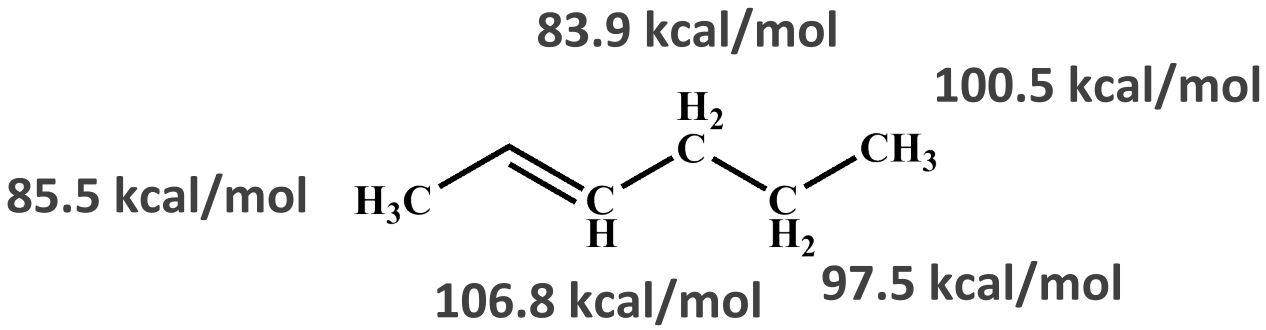


Motivation: Study the Influence of C=C Position on Low-Temperature Autoignition Chemistry using Hexene

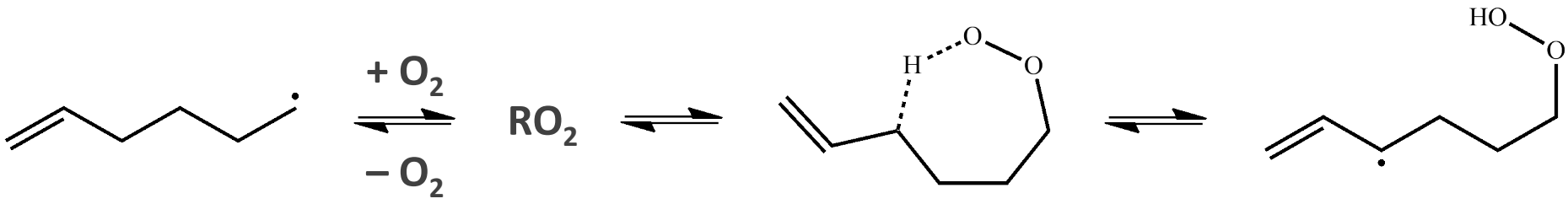




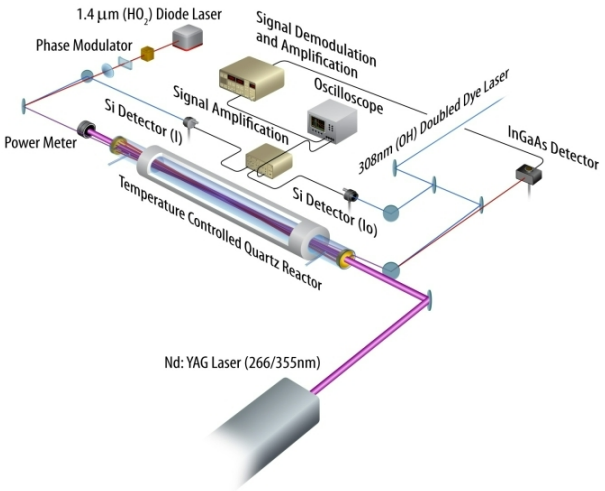
C=C Position Affects Distribution of Allylic, 1°, 2° C–H Bonds, Alters Reaction Pathways, Introduces Resonance

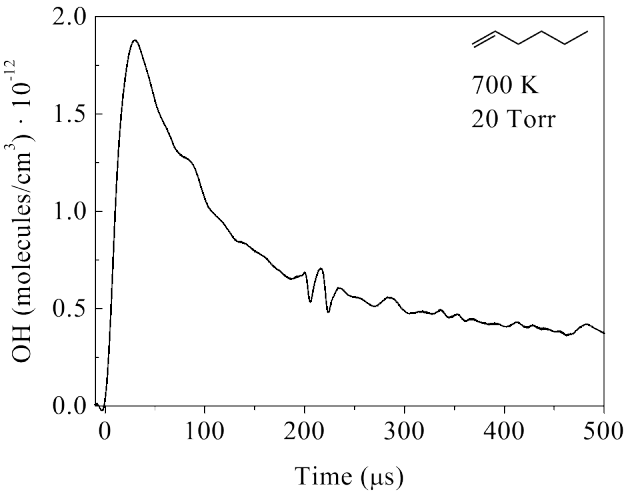


(E)-2-hexene C–H bond dissociation energies

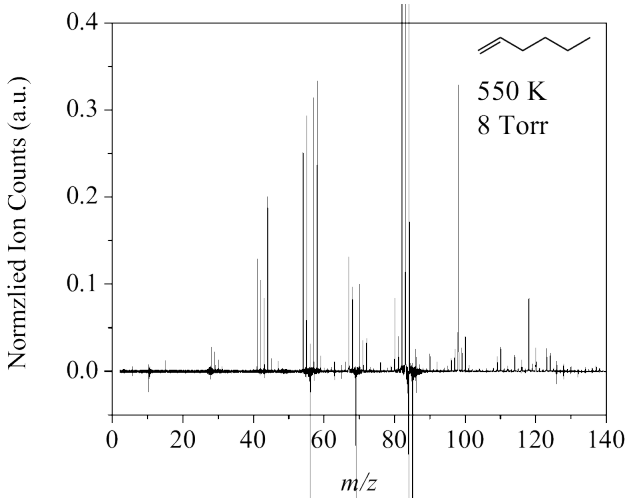


Experimental and Computational Approach





Multi-pass Infrared-Absorption Detection of OH, HO_2



Time-Dependent Photoionization Mass Spectra