SAND2016-6699C

Low Temperature Oxidation Studies of Butanone

Rebecca L Caravan, Brandon Rotavera, Krupa Ramasesha, David L Osborn & Craig A Taatjes

Combustion Chemistry Department, Combustion Research Facility, Sandia National Laboratories, CA

24th International Symposium on Gas Kinetics and Related Phenomena

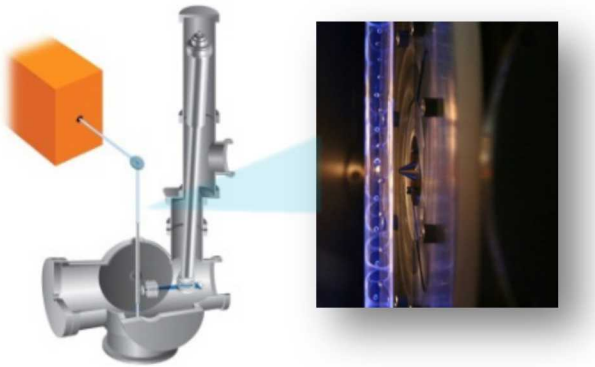
York, UK, July 21, 2016

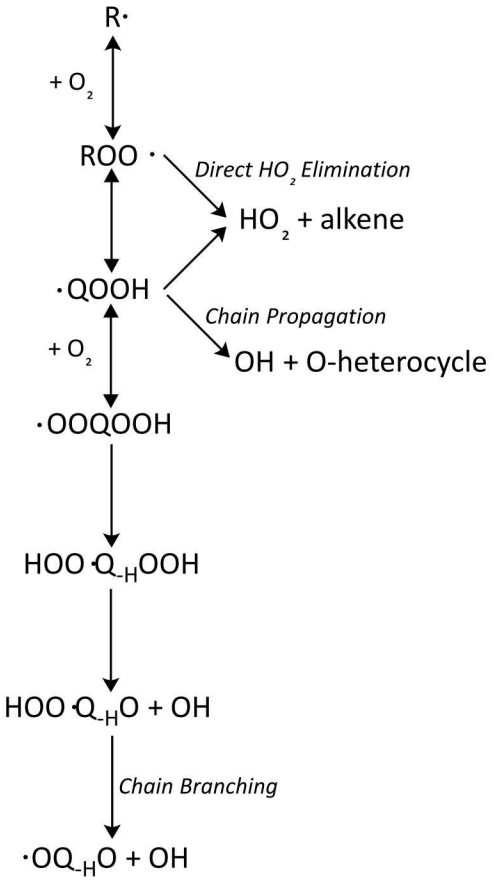
Sandia National Laboratories

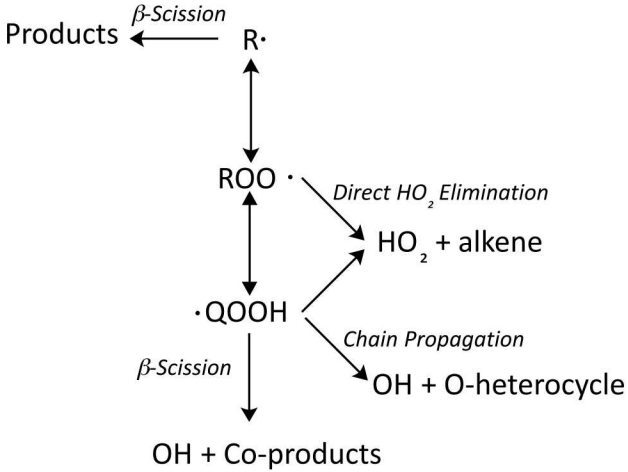
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

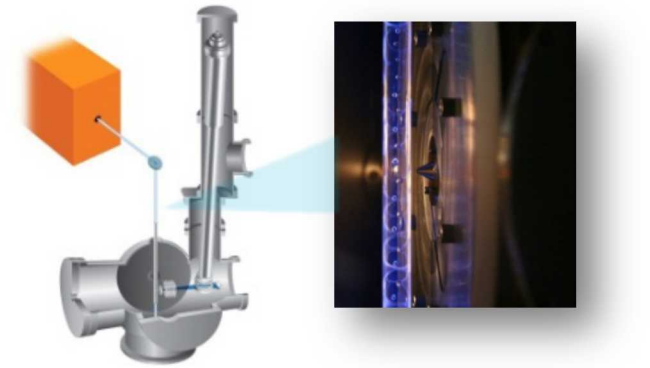
2-butanone

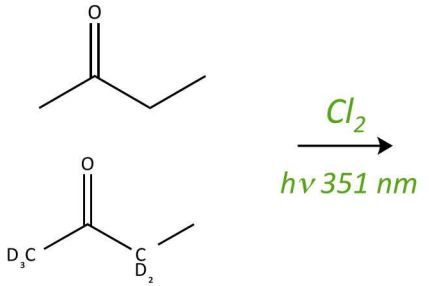
- Some previous interest in 2-butanone, mostly high T.
- Recent studies by Tranter & Walker, Burke et al, Dagaut.
- In particular we will examine R + O2 chemistry in the 500-700 K regime.
- Resonance stabilization of some R/QOOH radicals – different chemistry in competition with ROO/QOOH chemistry ?

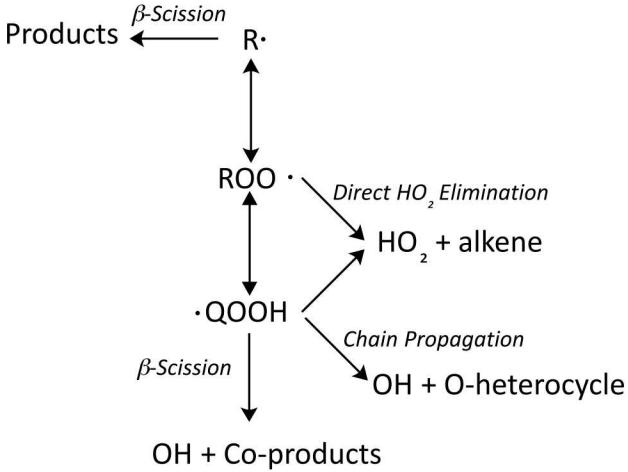


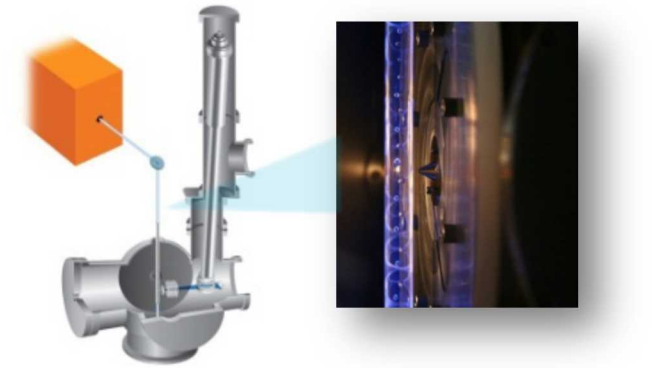

R·
+ O2
ROO ·
Direct HO2 Elimination
HO2 + alkene
·QOOH
Chain Propagation
+ O2
OH + O-heterocycle
·OOQOOH
HOO·Q-HOOH
HOO·Q-HO + OH
Chain Branching
·OQ-HO + OH

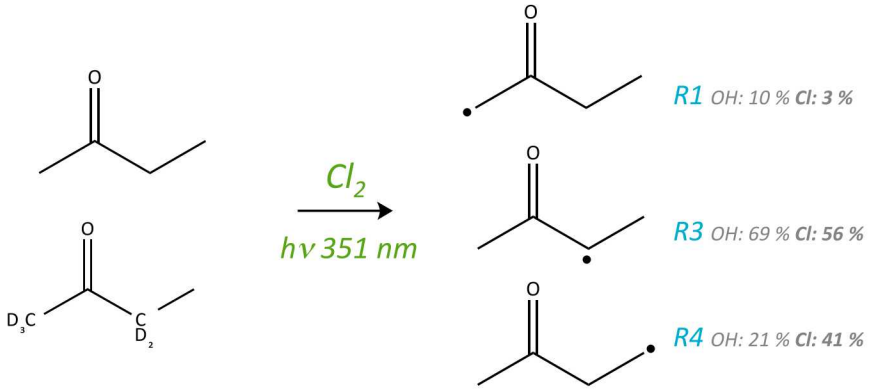

Products
β-Scission
R·
ROO ·
Direct HO2 Elimination
HO2 + alkene
·QOOH
Chain Propagation
β-Scission
OH + O-heterocycle
OH + Co-products

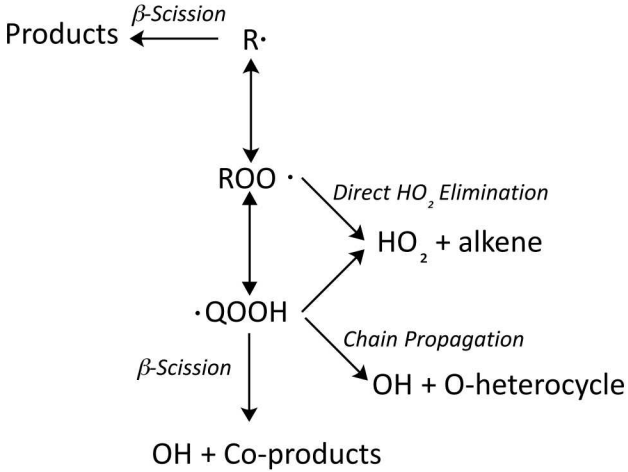


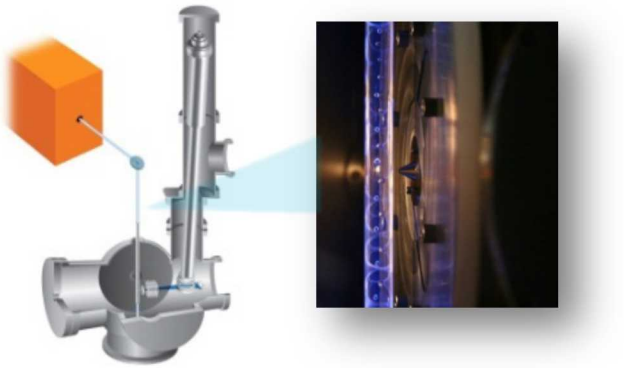

O
O
D3C
C
D2
Cl2
hν 351 nm


Products
β-Scission
R·
ROO ·
Direct HO2 Elimination
HO2 + alkene
·QOOH
Chain Propagation
OH + O-heterocycle
β-Scission
OH + Co-products

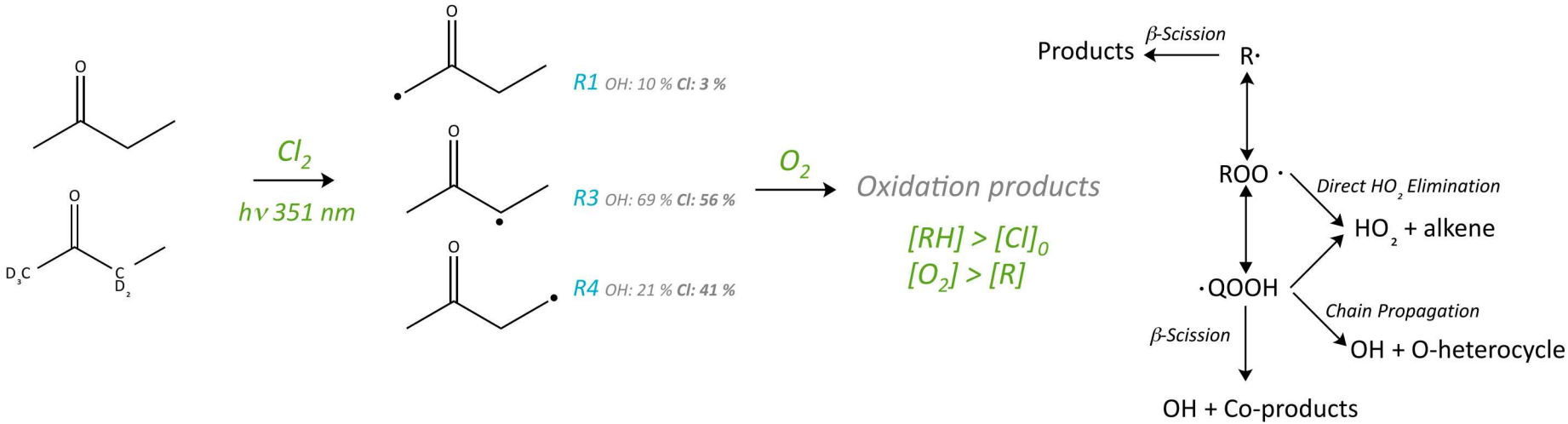


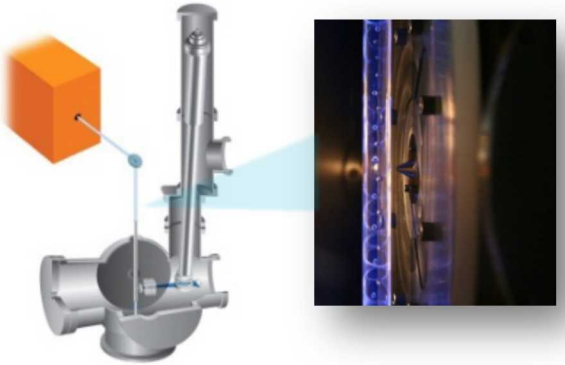




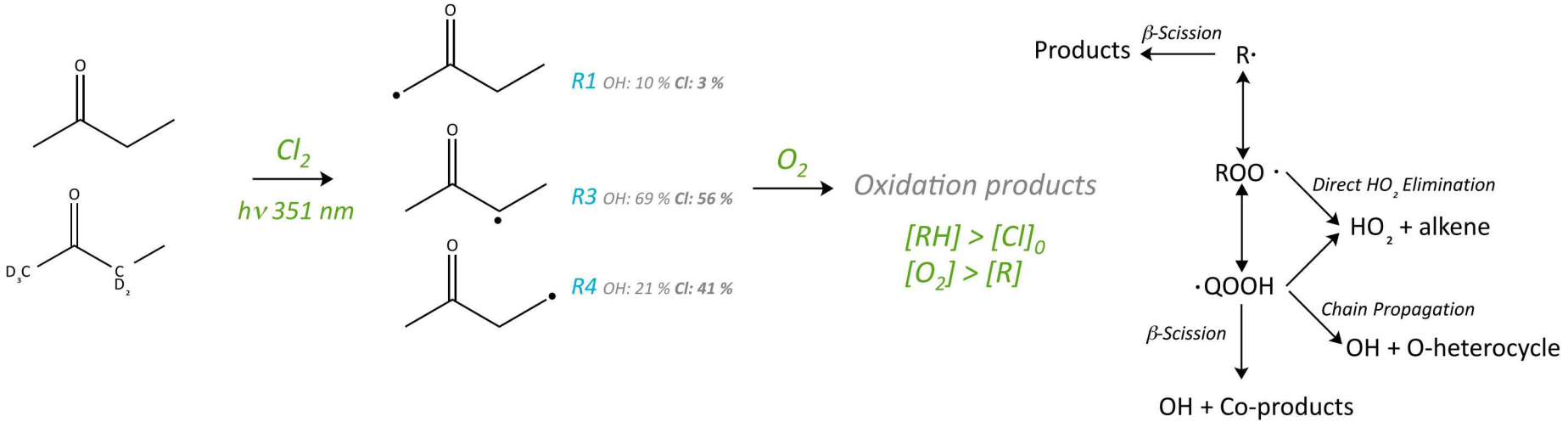


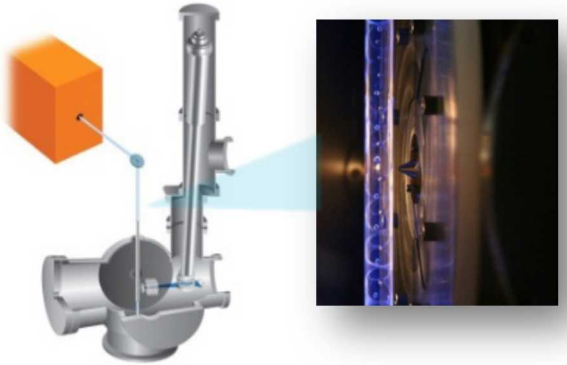
C.-W. Zhou *et al.*,*Phys. Chem. Chem. Phys.*, **2011**, *13*, 11175–11192





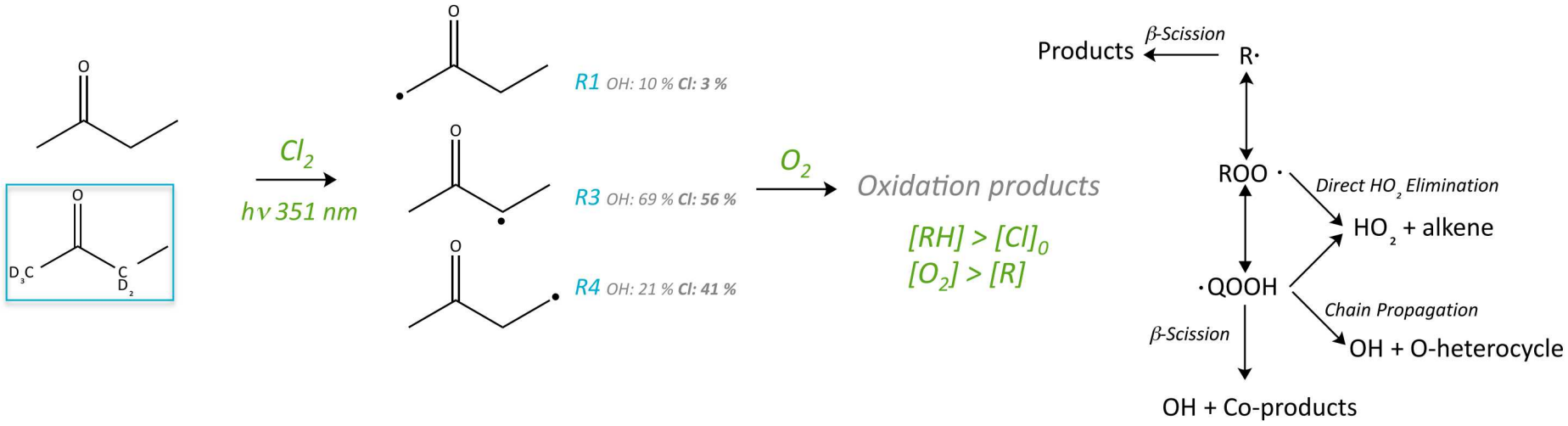
C.-W. Zhou *et al.*,*Phys. Chem. Chem. Phys.*, **2011**, *13*, 11175–11192

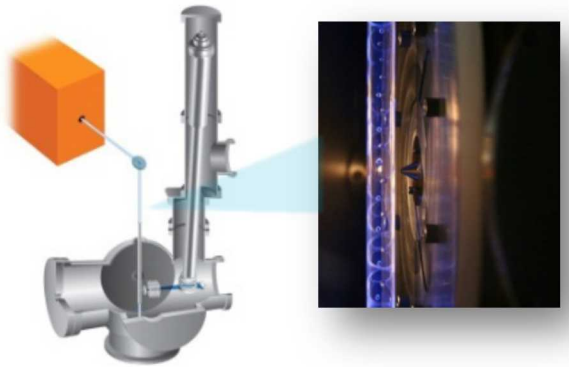




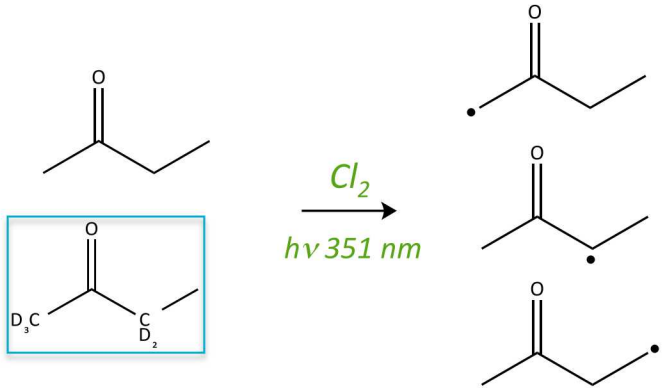
Species	*Number Density (molecules/cm^3)*	
2-butanone, 2 butanone-*D5*	$1.4 \cdot 10^{14}$	500 K & 700 K, 10 Torr
O_2	$2.9 \cdot 10^{16}$ (18-28 %)	$[RH]/[Cl_0]$:18-24
Cl (Cl_2 photolysis, 351 nm)	$5.9\text{-}8.2 \cdot 10^{12}$	$[O_2]/[Cl_0]$: 3528-4870
He	$1.0\text{-}1.7.10^{17}$	Parent depletion 1.5-2.1 %

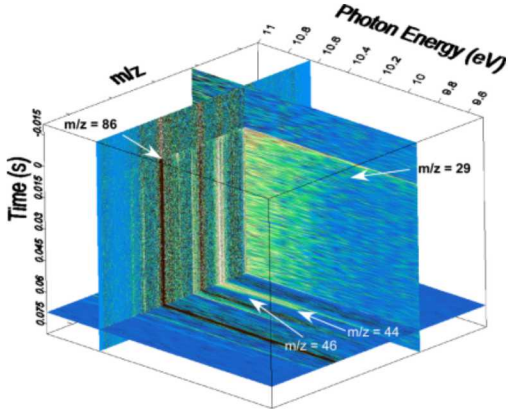
C.-W. Zhou *et al.*,*Phys. Chem. Chem. Phys.*, **2011**, *13*, 11175–11192

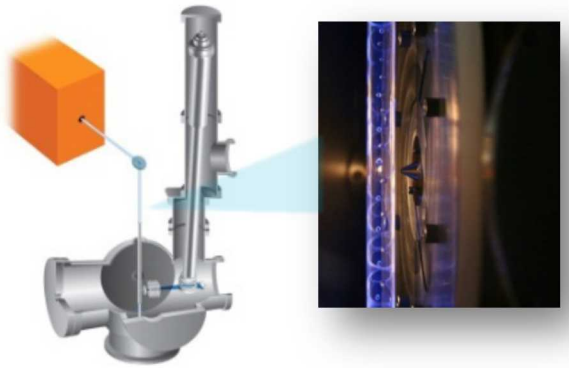




Species	*Number Density (molecules/cm^3)*	
2-butanone, 2 butanone-*D5*	$1.4 \cdot 10^{14}$	500 K & 700 K, 10 Torr
O_2	$2.9 \cdot 10^{16}$ (18-28 %)	$[RH]/[Cl_0]$:18-24
Cl (Cl_2 photolysis, 351 nm)	$5.9\text{-}8.2 \cdot 10^{12}$	$[O_2]/[Cl_0]$: 3528-4870
He	$1.0\text{-}1.7.10^{17}$	Parent depletion 1.5-2.1 %



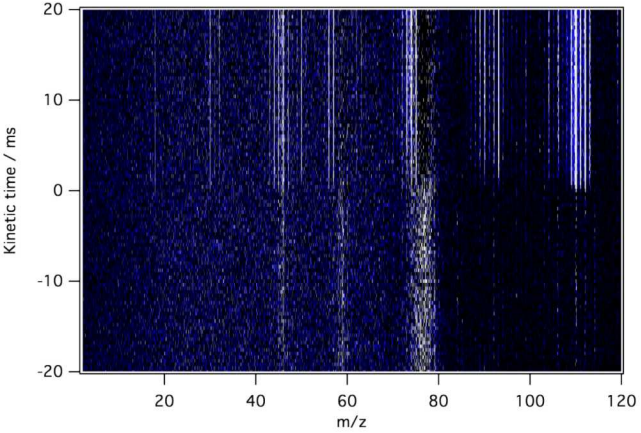




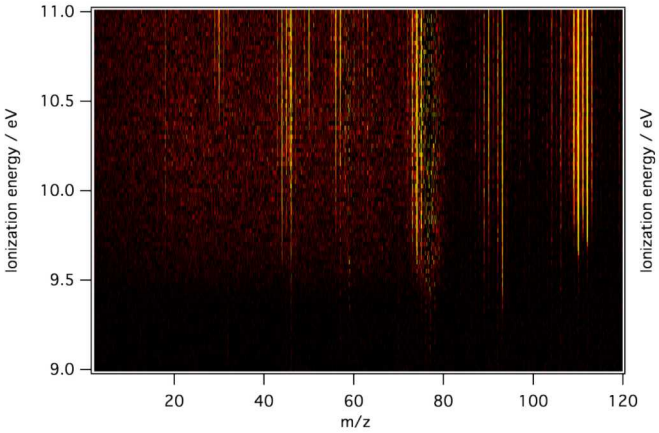
Species	Number Density (molecules/cm^3)	
2-butanone, 2 butanone-*D5*	$1.4 \cdot 10^{14}$	500 K & 700 K, 10 Torr
O_2	$2.9 \cdot 10^{16}$ (18-28 %)	$[RH]/[Cl_0]$:18-24
Cl (Cl_2 photolysis, 351 nm)	$5.9\text{-}8.2 \cdot 10^{12}$	$[O_2]/[Cl_0]$: 3528-4870
He	$1.0\text{-}1.7.10^{17}$	Parent depletion 1.5-2.1 %

C.-W. Zhou *et al.*,*Phys. Chem. Chem. Phys.*, **2011**, *13*, 11175–11192

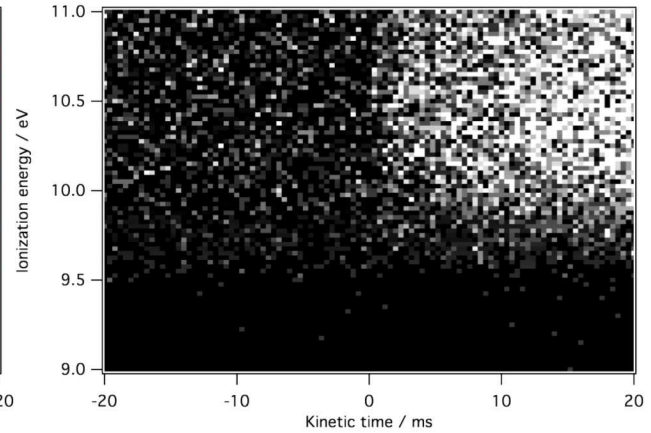
XT : Temporal evolution of m/z over a given energy range

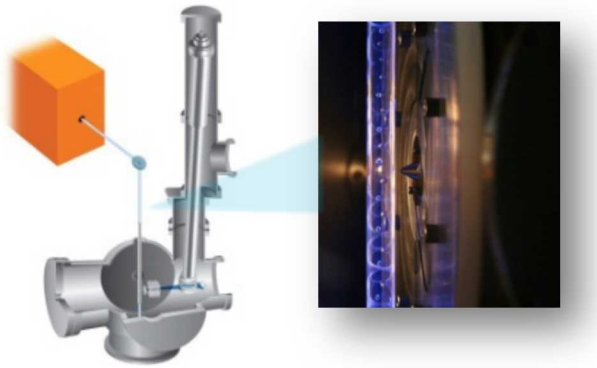


EX: Isomers resolution over a given kinetic time range



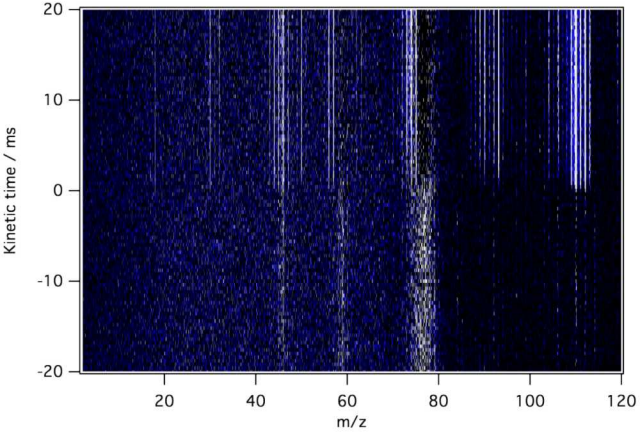
ET: Temporal evolution of isomers over a given m/z range



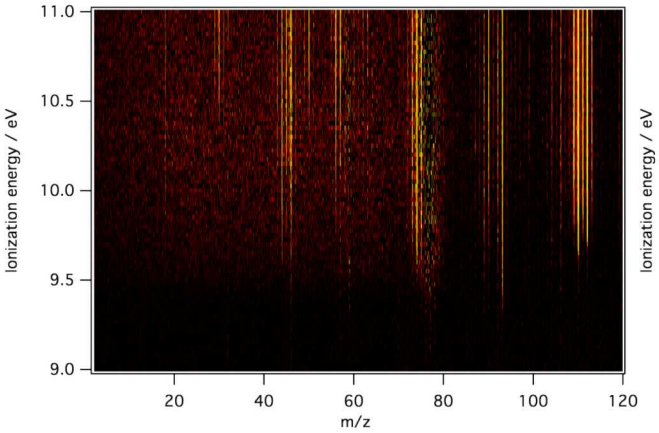


Species	*Number Density (molecules/cm^3)*	
2-butanone, 2 butanone-*D5*	$1.4 \cdot 10^{14}$	500 K & 700 K, 10 Torr
O_2	$2.9 \cdot 10^{16}$ (18-28 %)	$[RH]/[Cl_0]$:18-24
Cl (Cl_2 photolysis, 351 nm)	$5.9\text{-}8.2 \cdot 10^{12}$	$[O_2]/[Cl_0]$: 3528-4870
He	$1.0\text{-}1.7 \cdot 10^{17}$	Parent depletion 1.5-2.1 %

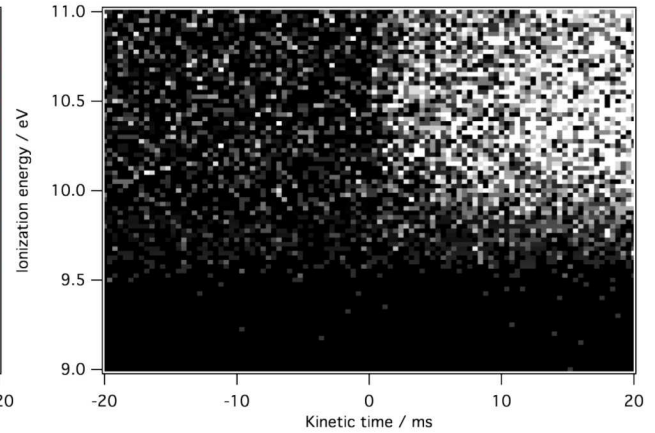
XT : Temporal evolution of m/z over a given energy range



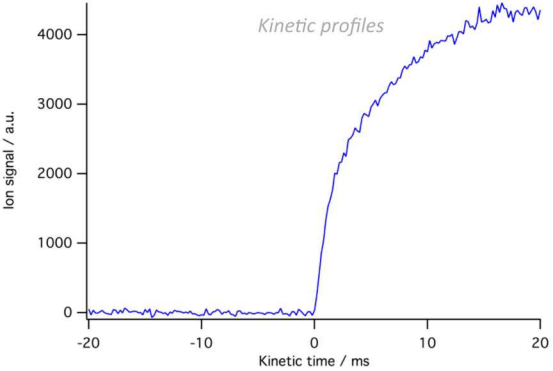
EX: Isomers resolution over a given kinetic time range



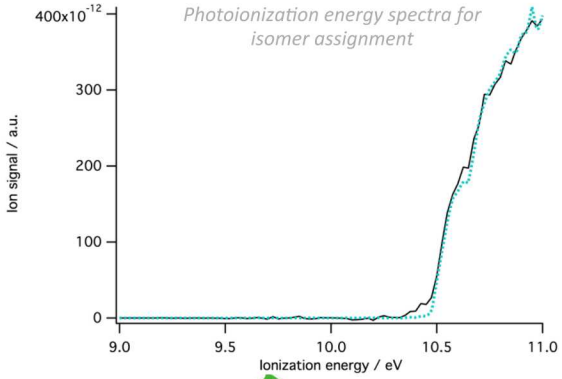
ET: Temporal evolution of isomers over a given m/z range



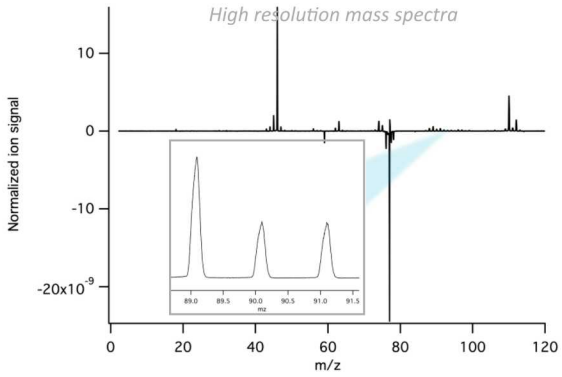
Kinetic profiles



Photoionization energy spectra for isomer assignment

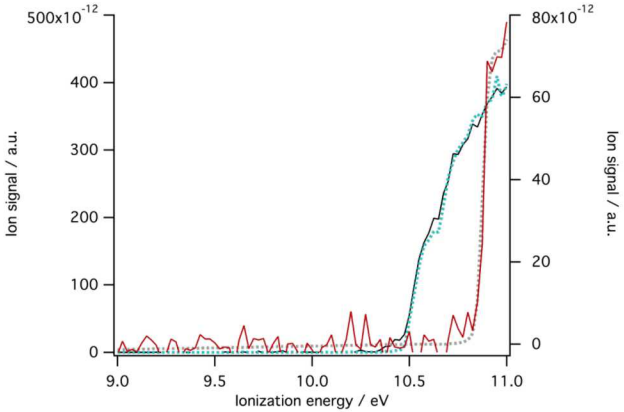


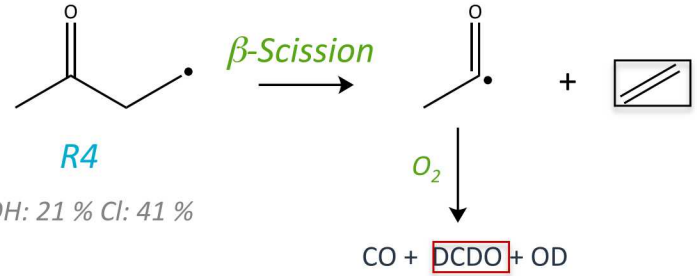
High resolution mass spectra



R3

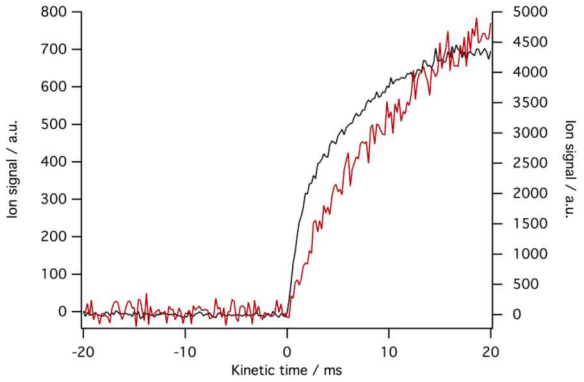
OH: 69 % Cl: 56 %

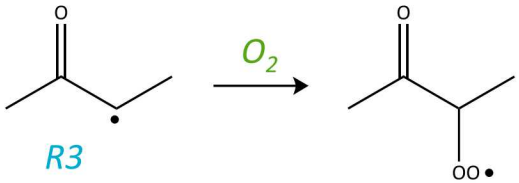




R4

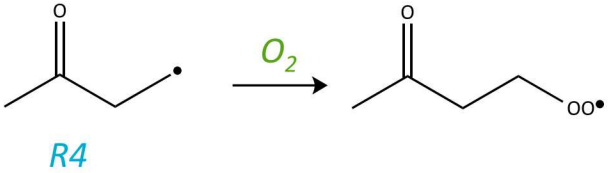
OH: 21 % Cl: 41 %





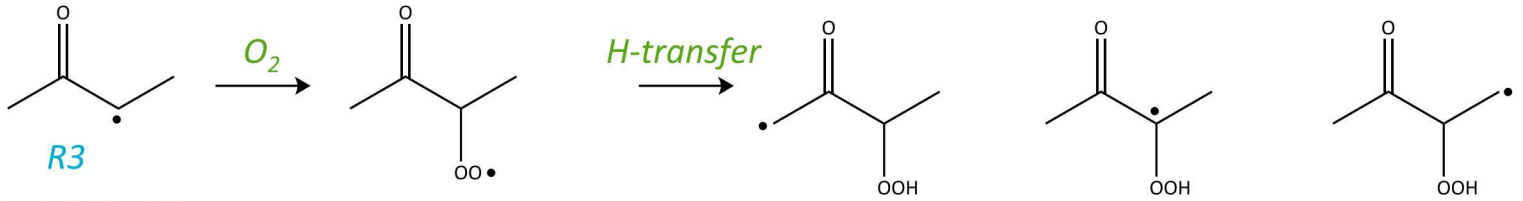
R3

OH: 69 % Cl: 56 %



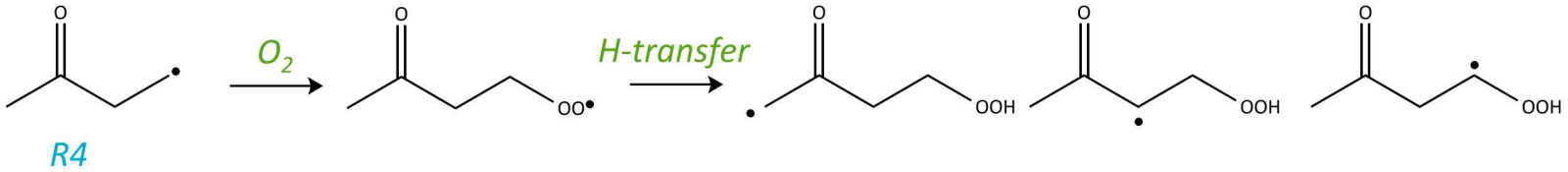
R4

OH: 21 % Cl: 41 %



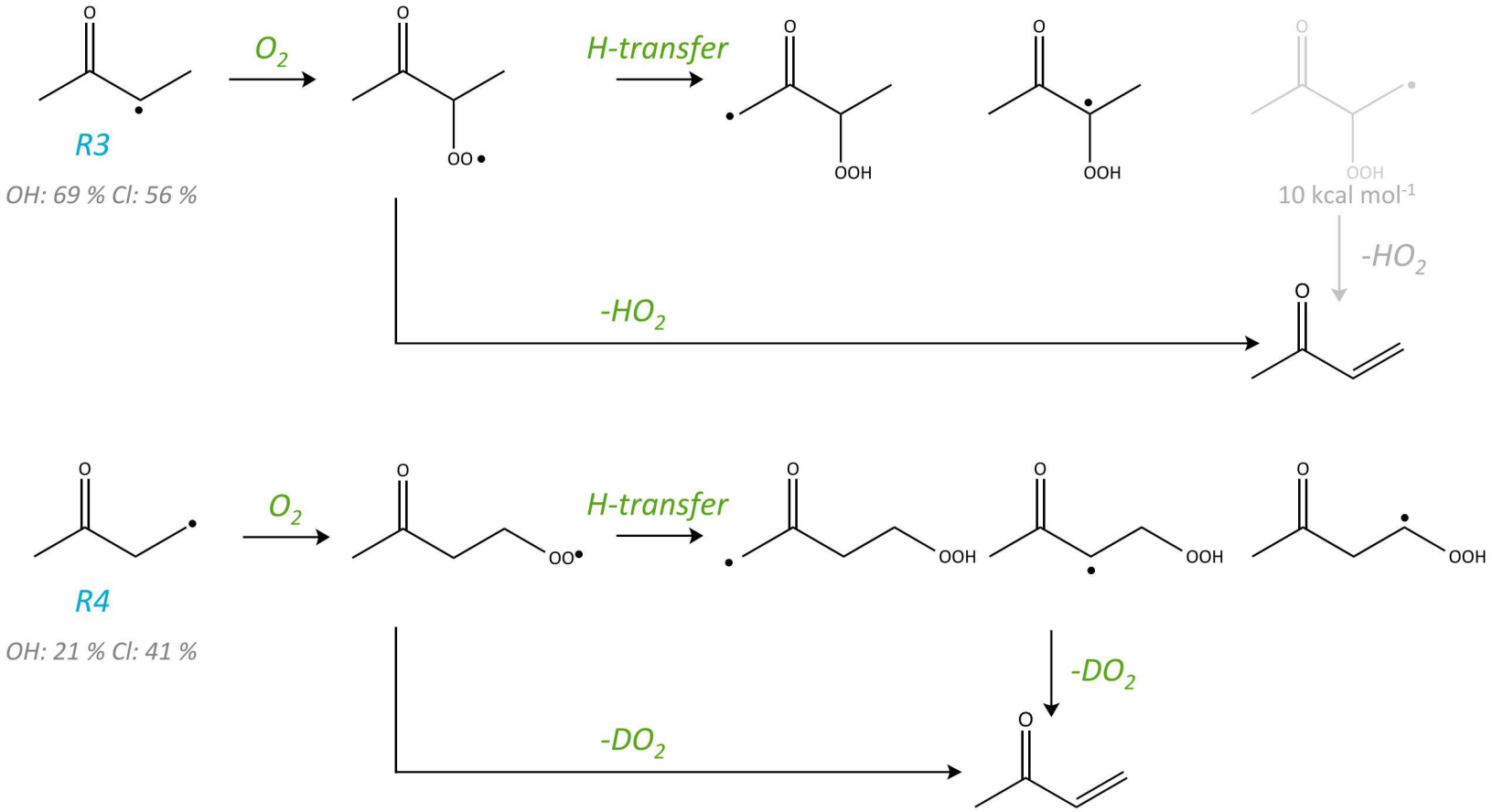
R3

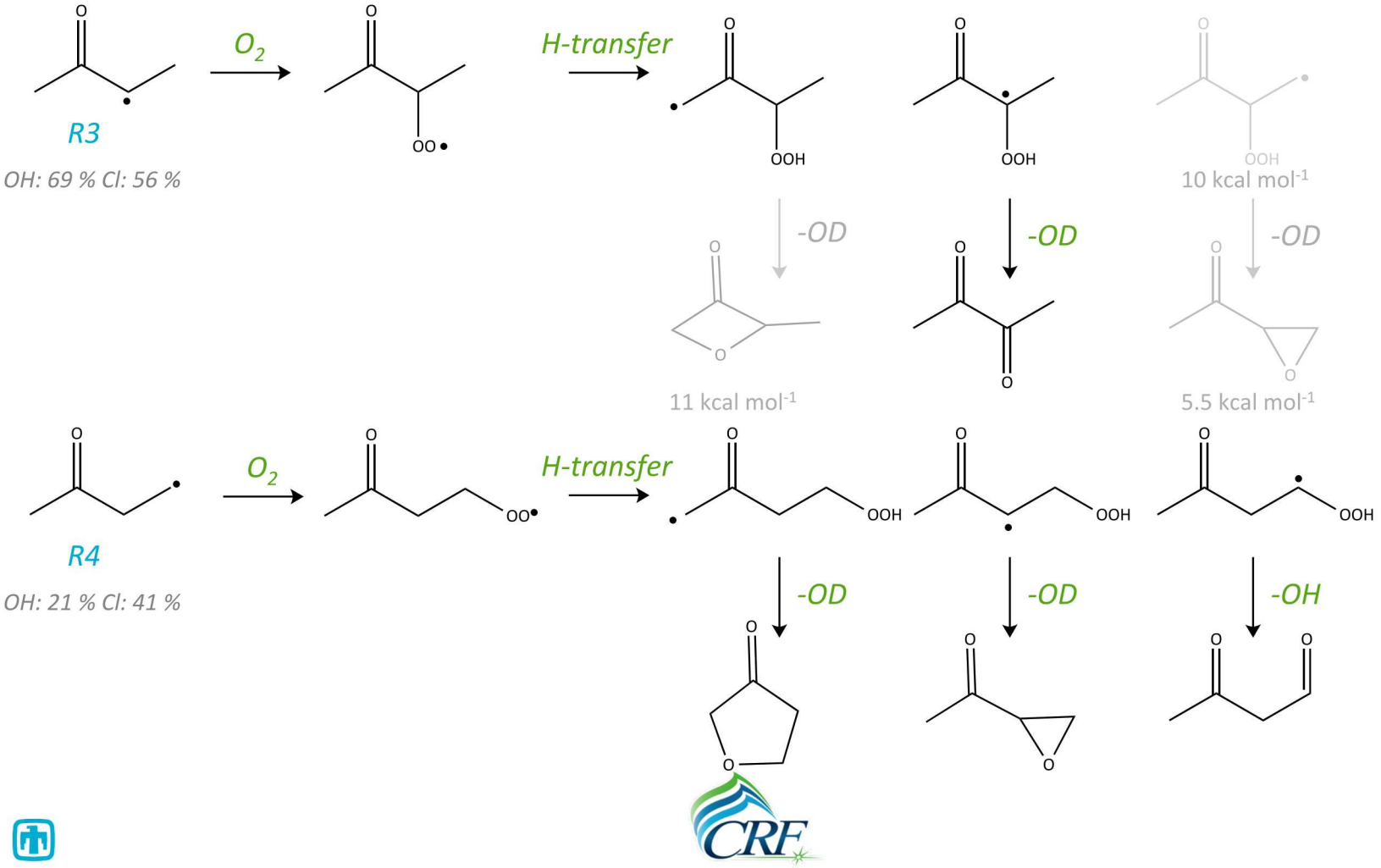
OH: 69 % Cl: 56 %

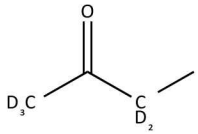


R4

OH: 21 % Cl: 41 %

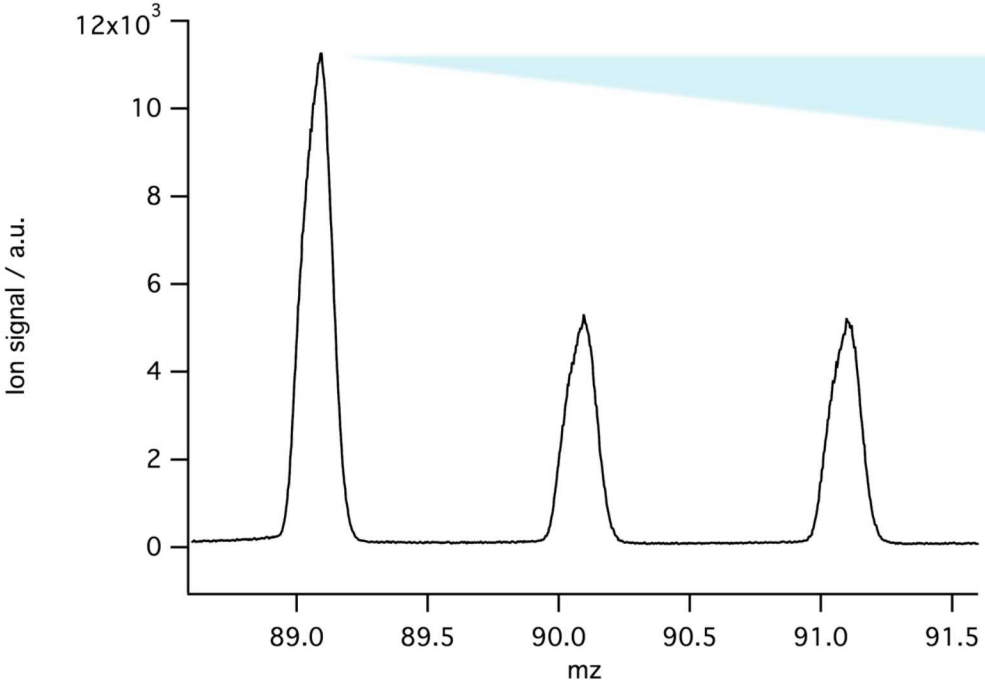

R3
OH: 69 % Cl: 56 %
O2
H-transfer
OOH
10 kcal mol-1
-HO2
-HO2
R4
OH: 21 % Cl: 41 %
O2
H-transfer
-DO2
-DO2

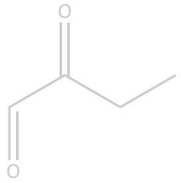

R3
OH: 69 % Cl: 56 %
O2
H-transfer
OOH
10 kcal mol-1
-OD
11 kcal mol-1
5.5 kcal mol-1
R4
OH: 21 % Cl: 41 %
-OH



Resolving the parent + 14 channels

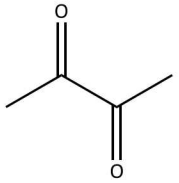
m/z 77



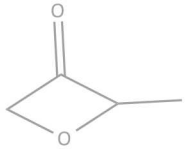


9.43 eV

R1: 3 %

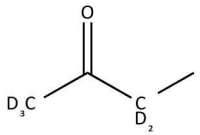


9.11 eV



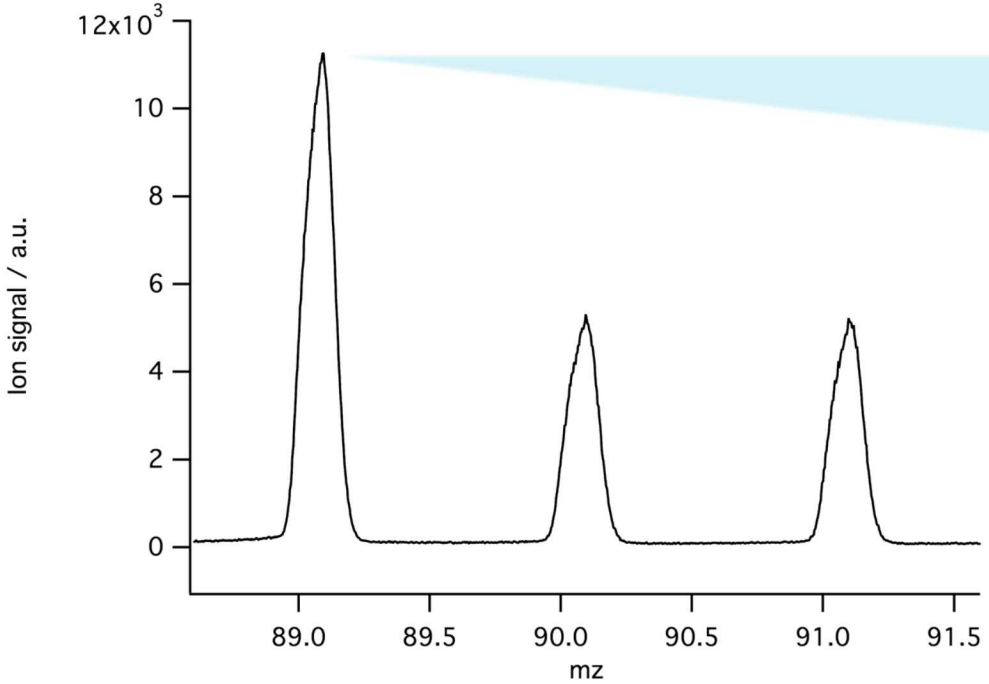
9.20 eV

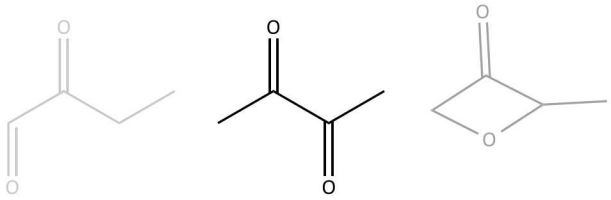
5.4/11 kcal mol^{-1}



Resolving the parent + 14 channels

m/z 77

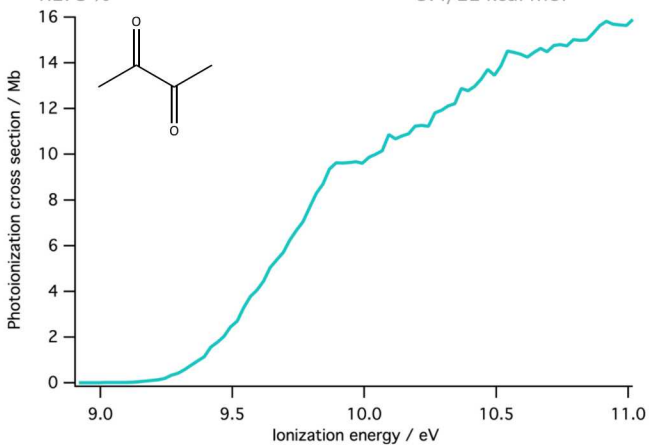




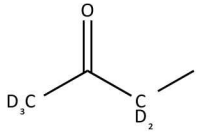
9.43 eV *9.11 eV* *9.20 eV*

R1: 3 %

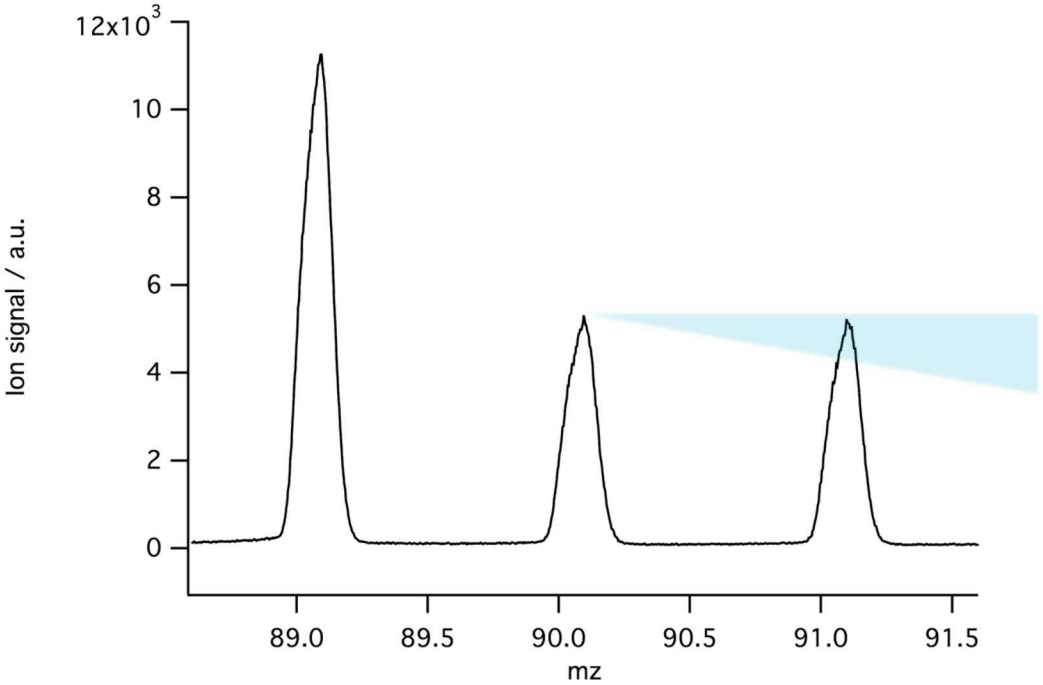
5.4/11 kcal mol^{-1}

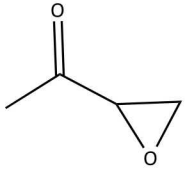


Resolving the parent + 14 channels

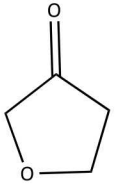


m/z 77

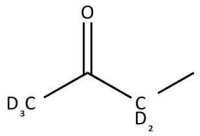




9.67 eV

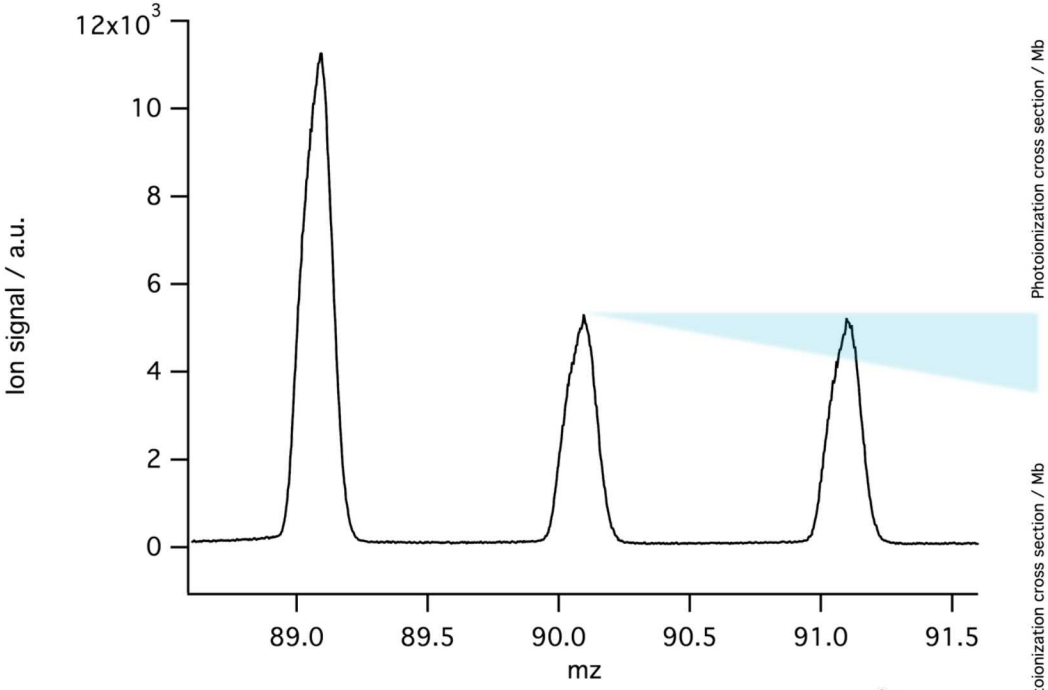


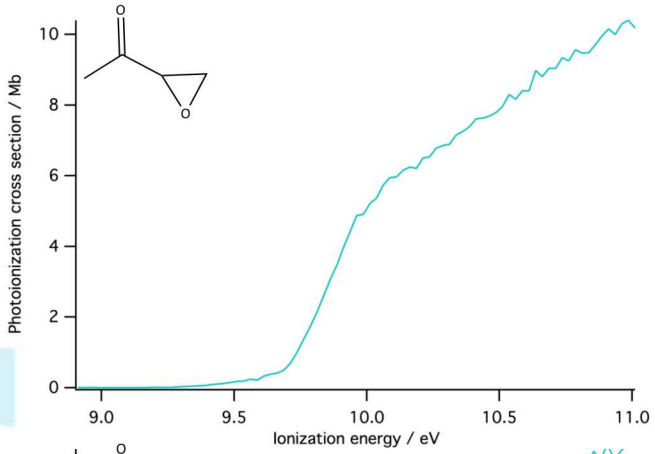
9.41 eV

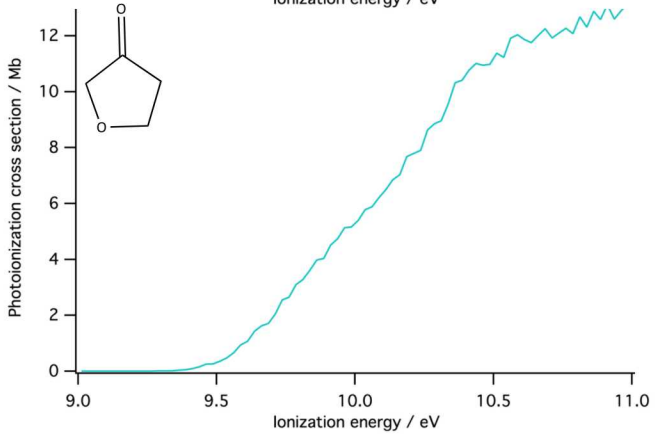


Resolving the parent + 14 channels

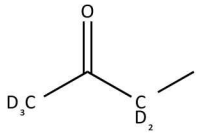
m/z 77



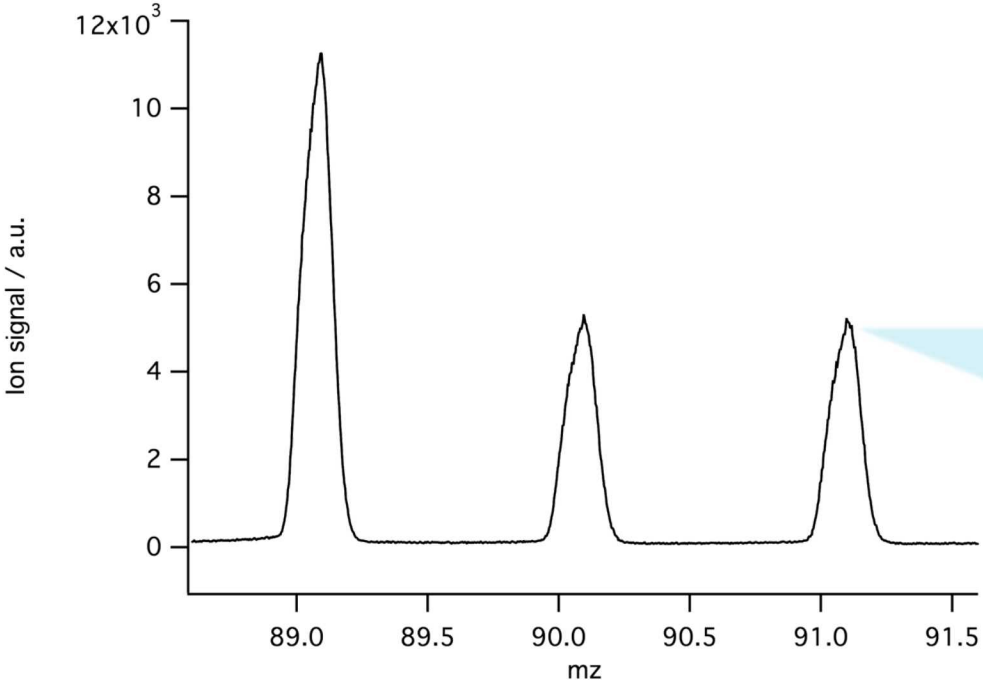


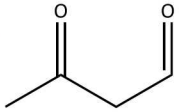


Resolving the parent + 14 channels

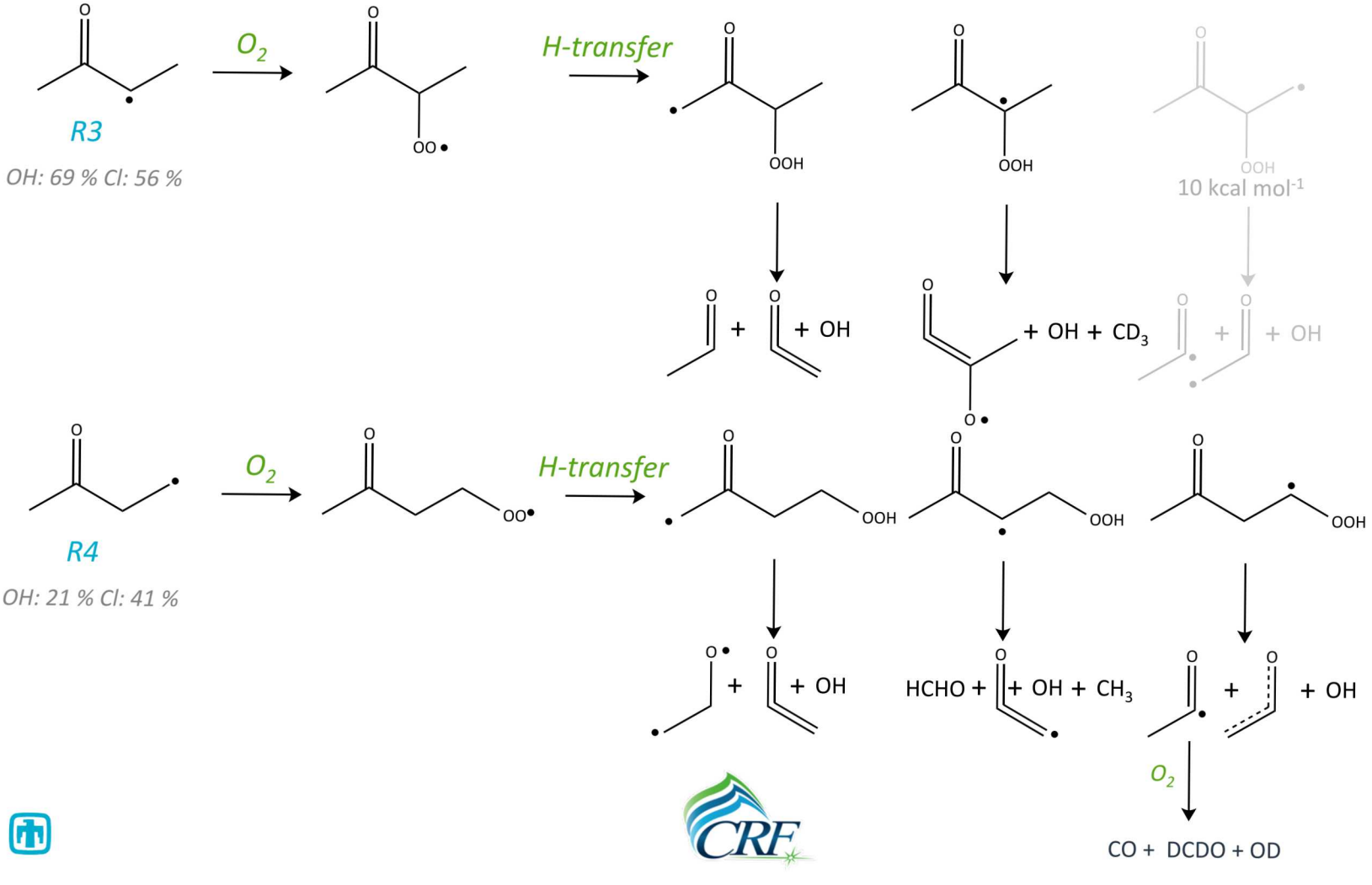


m/z 77

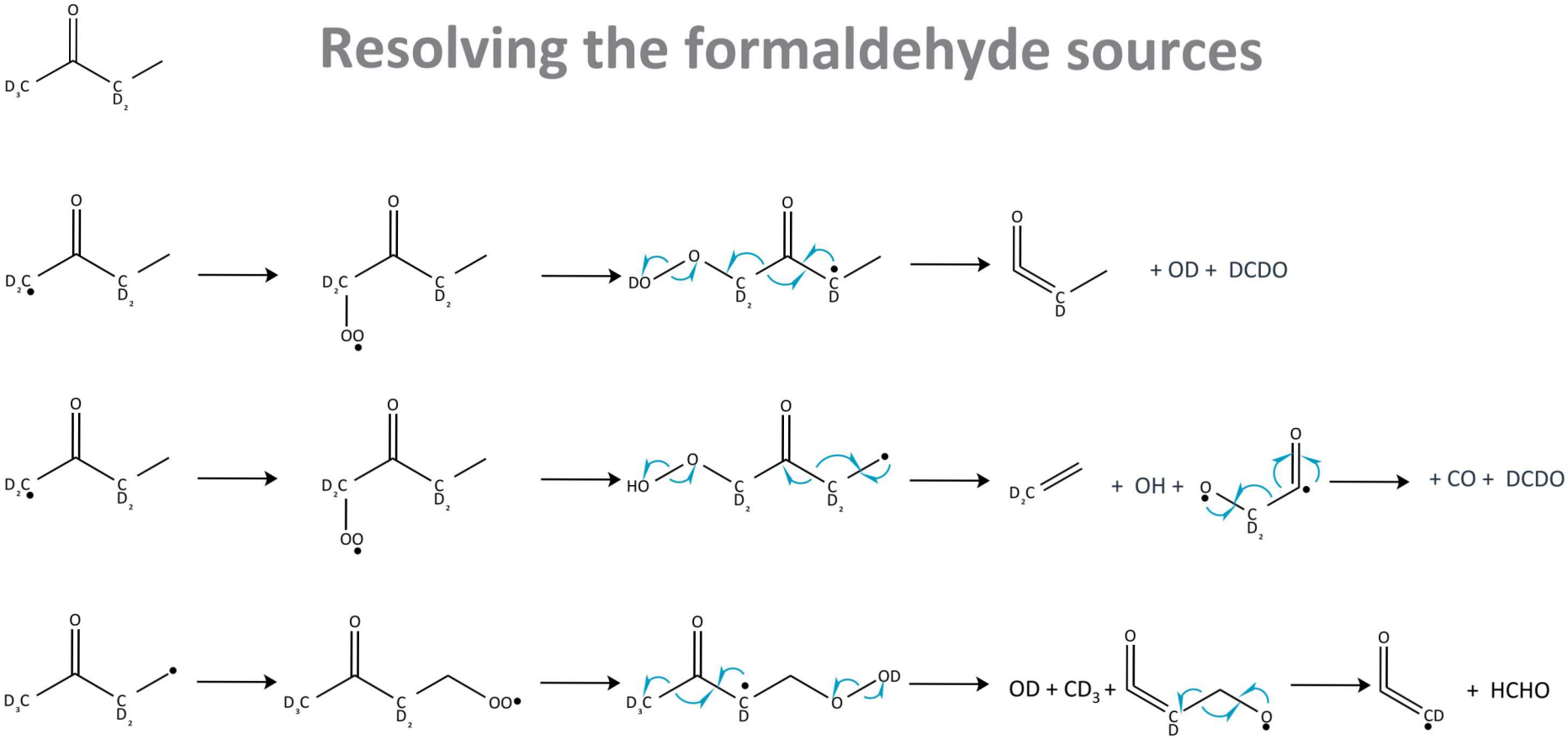




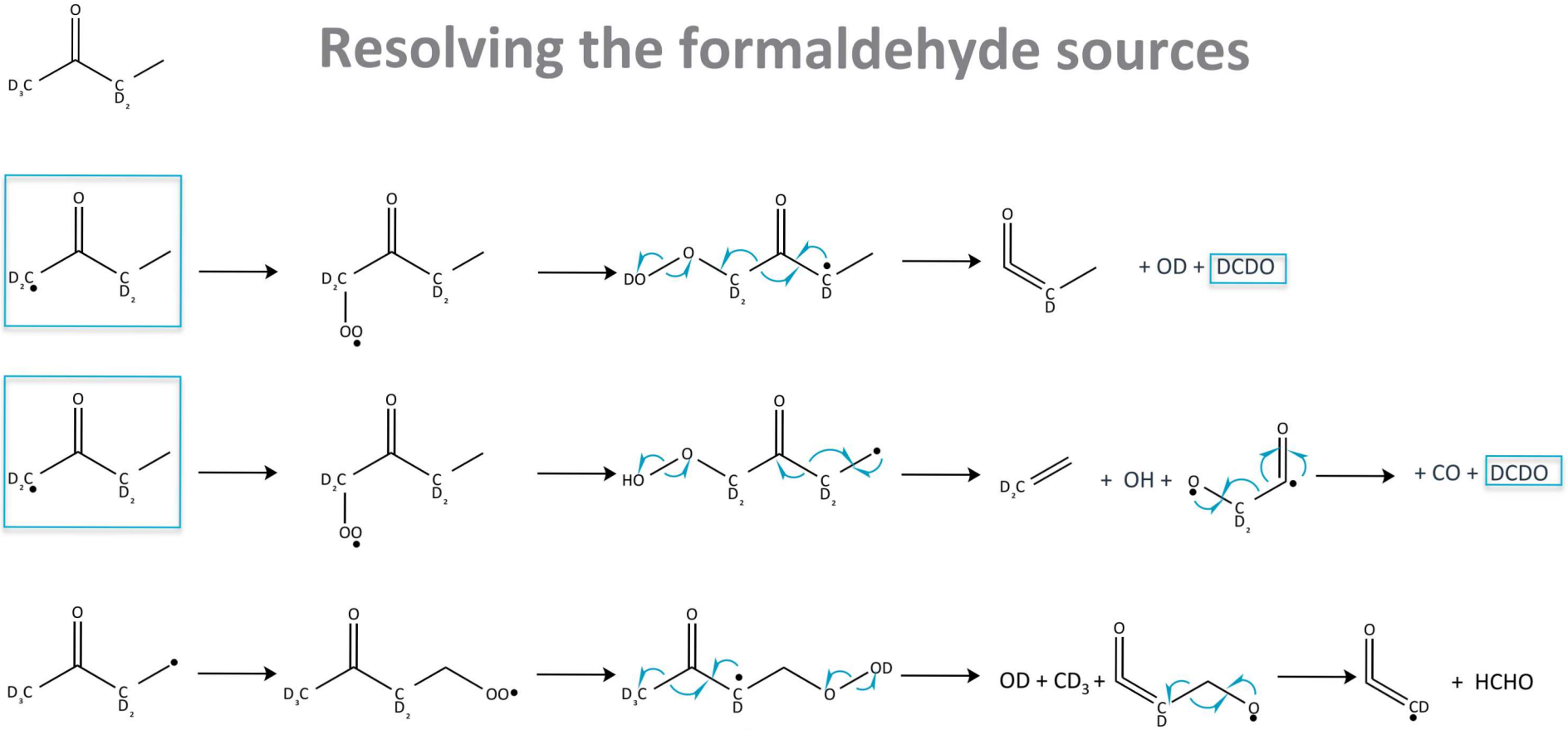
9.54 eV


R3
OH: 69 % Cl: 56 %
O2
H-transfer
OOH
10 kcal mol-1
+ OH
+ OH + CD3
R4
OH: 21 % Cl: 41 %
HCHO + + OH + CH3
+ OH
O2
CO + DCDO + OD

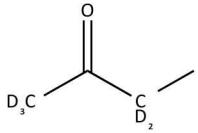
Resolving the formaldehyde sources

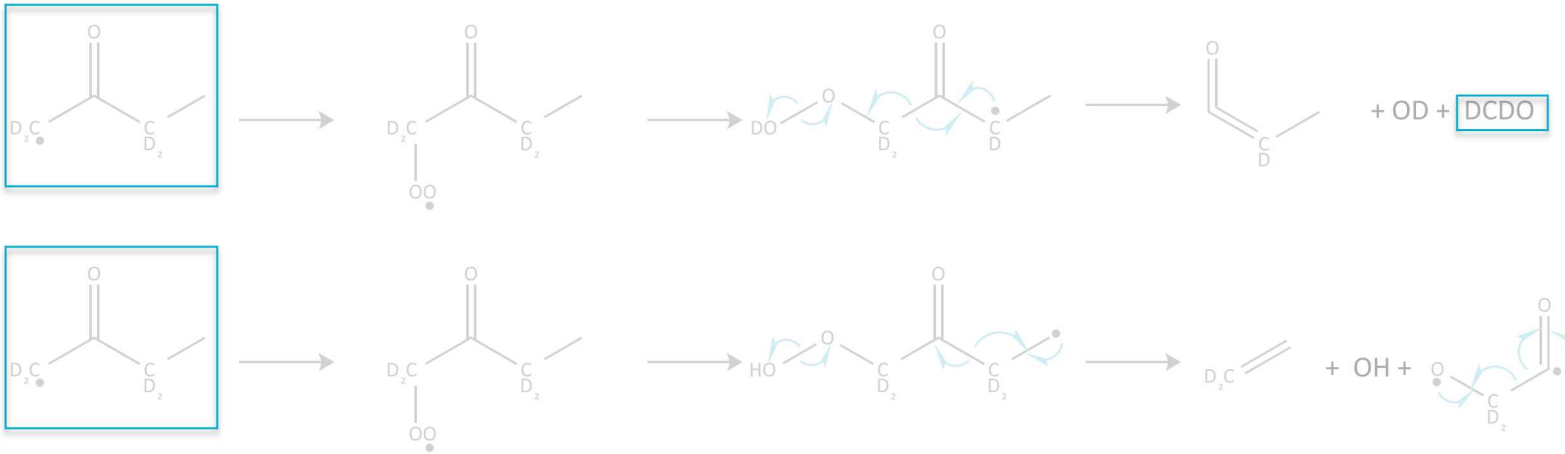


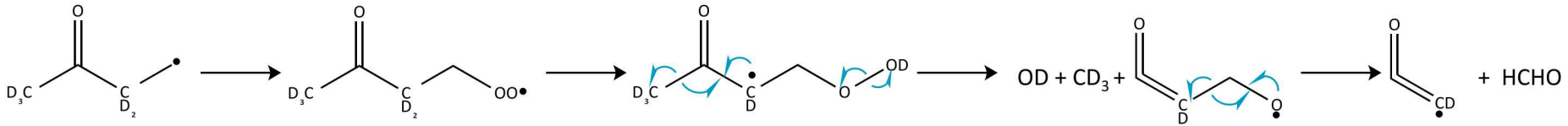
Resolving the formaldehyde sources



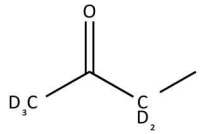
Resolving the formaldehyde sources

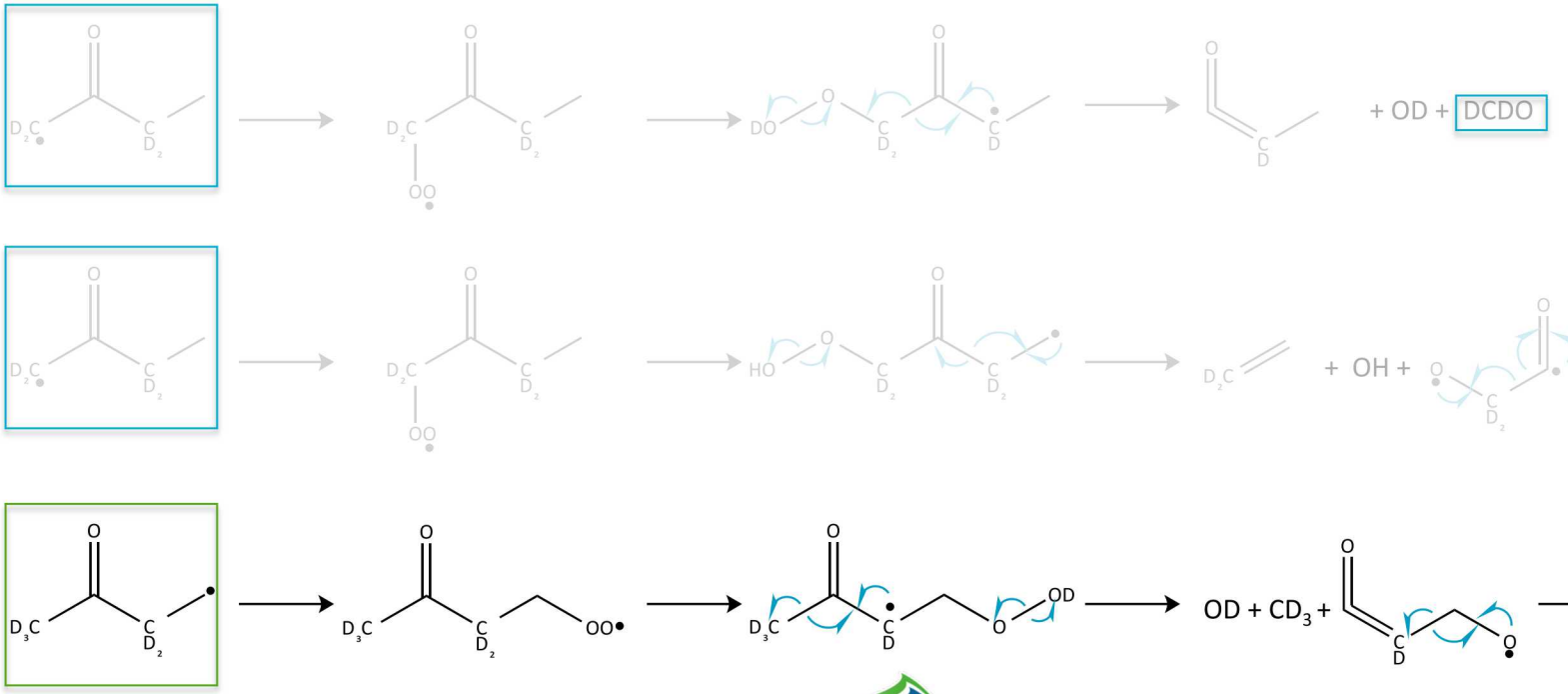




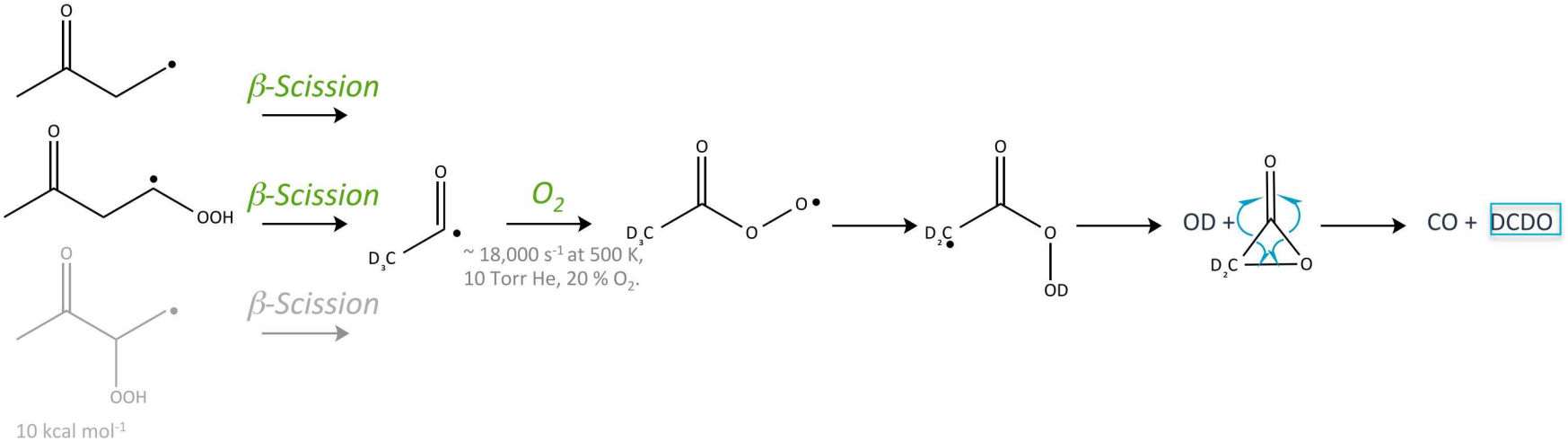


Resolving the formaldehyde sources



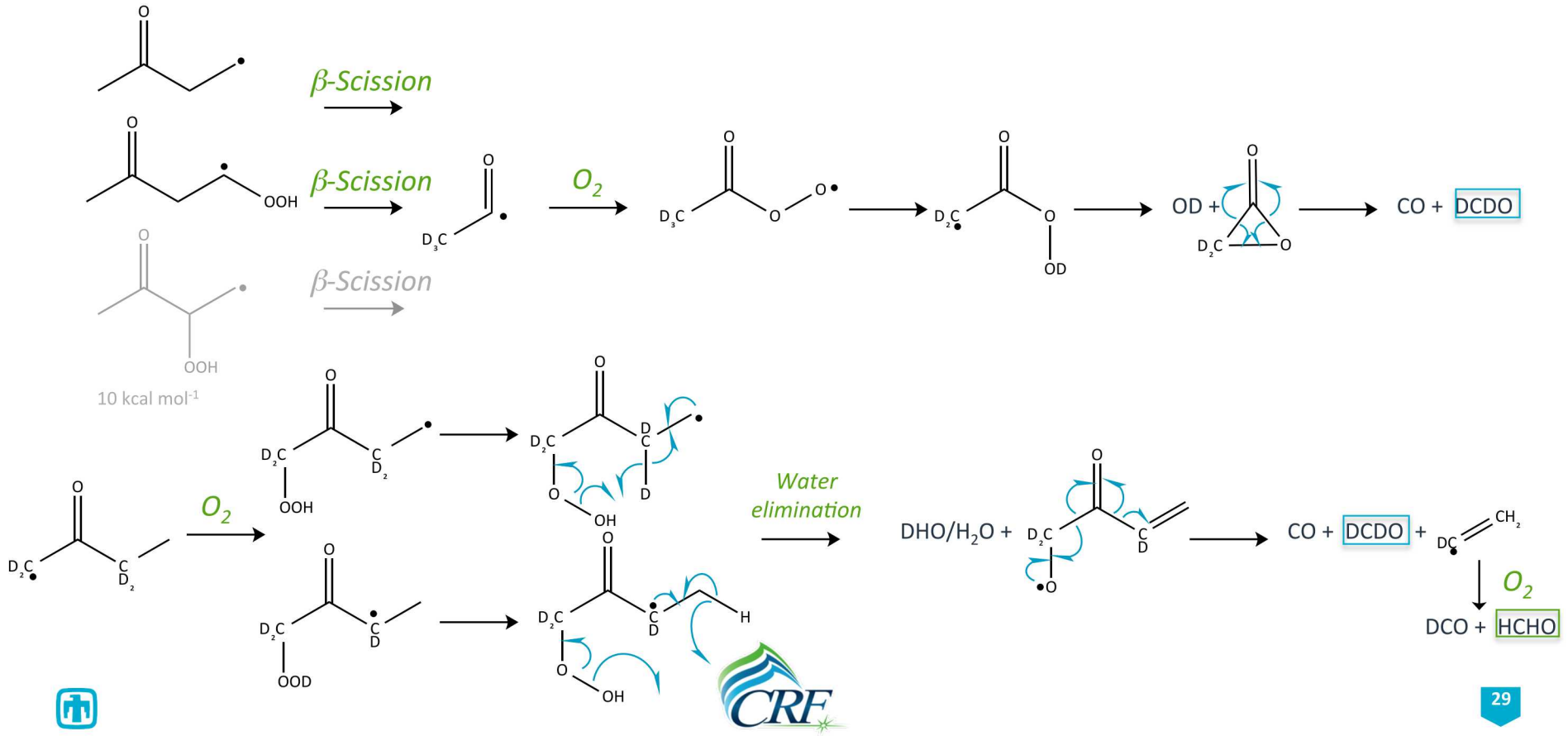


Additional potential formaldehyde sources

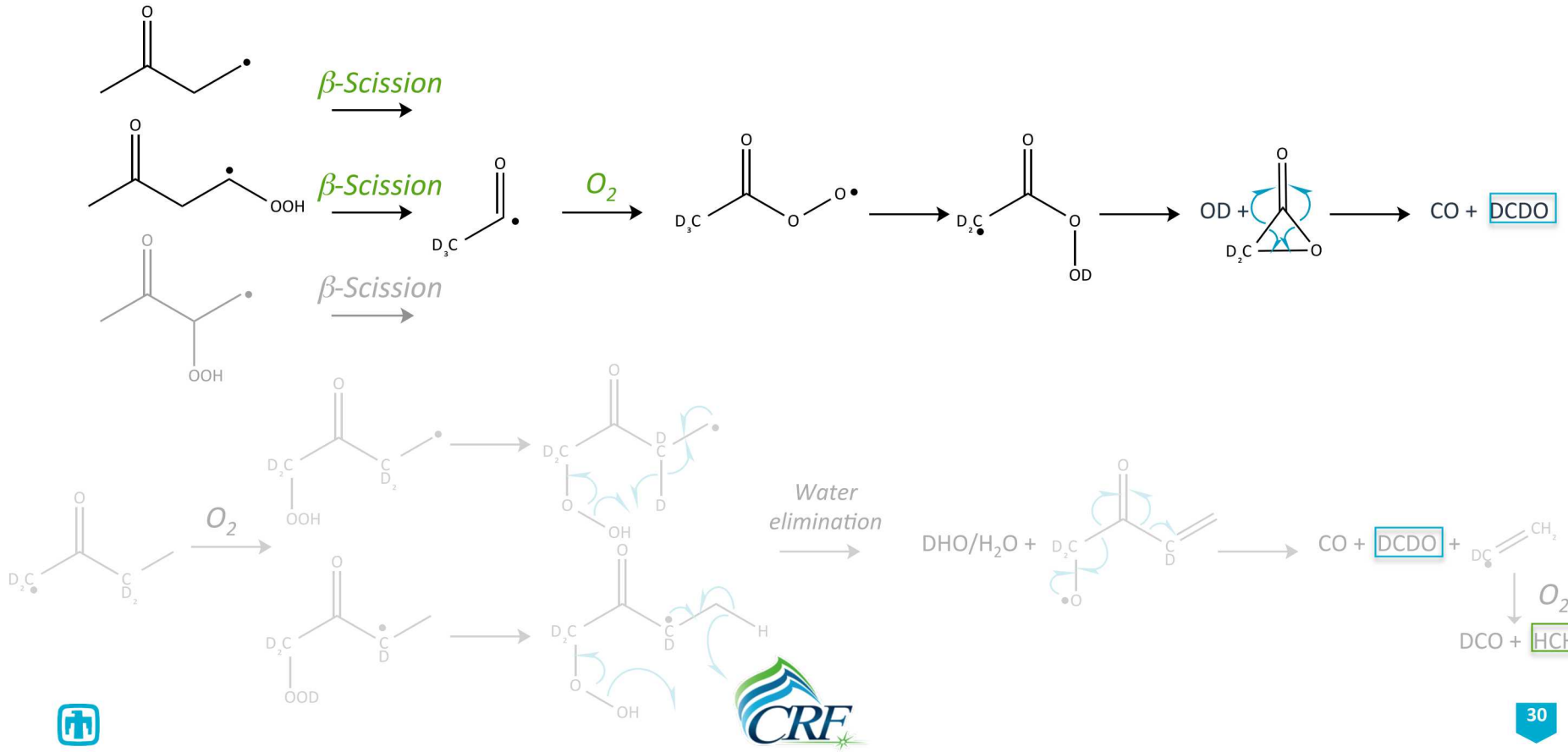


S J.. Carr *et al.*, *J. Phys. Chem. A*, **2011**, *115* (6),1069–1085
M. T. B. Romero *et al.*, *Faraday Discuss.*, **2005**, *130*, 73-88
N. I. Butkovskaya *et al.*, *J. Phys. Chem. A*, **2004**, *108*, 1160–1168.

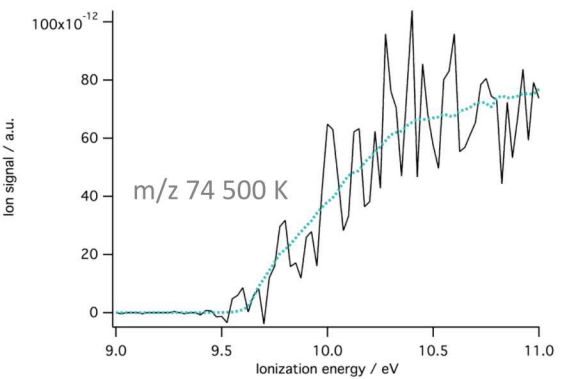
Additional potential formaldehyde sources

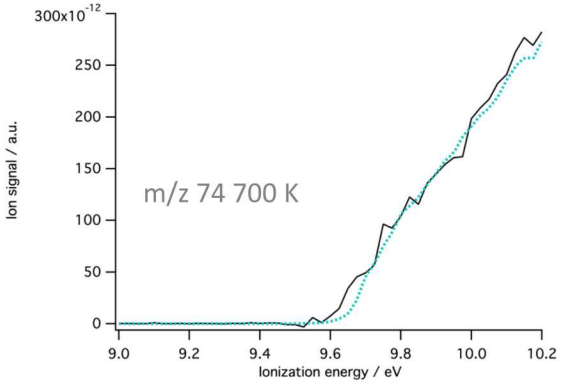


Additional potential formaldehyde sources

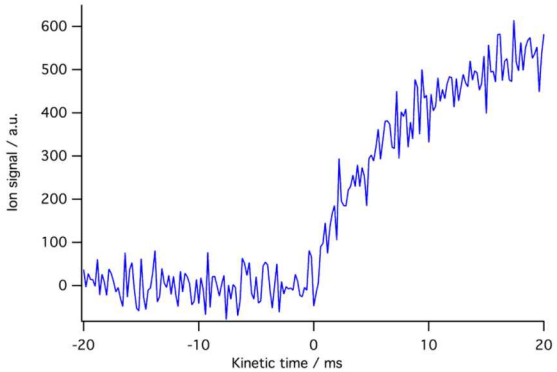


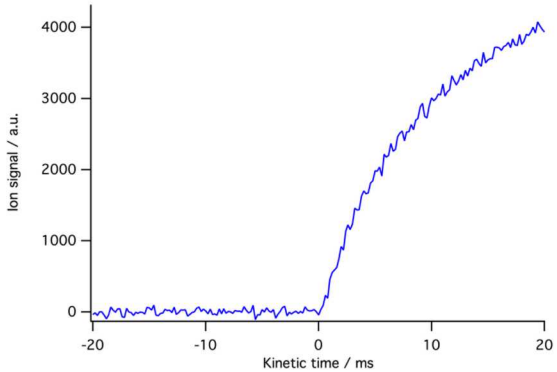
Methyl vinyl ketone



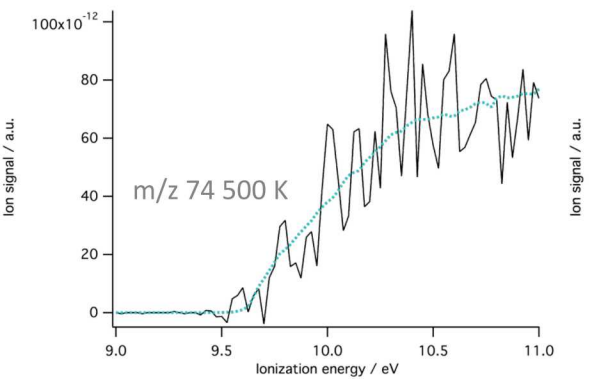


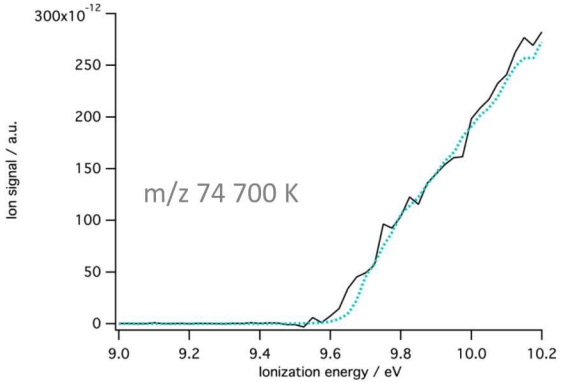
700 K/500 K: 10

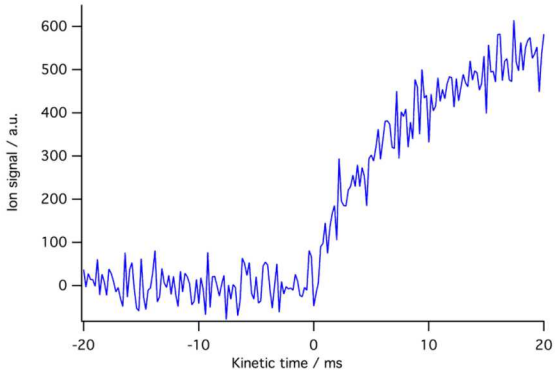


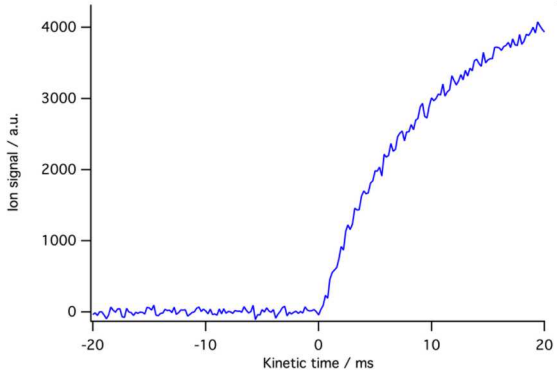


Methyl vinyl ketone

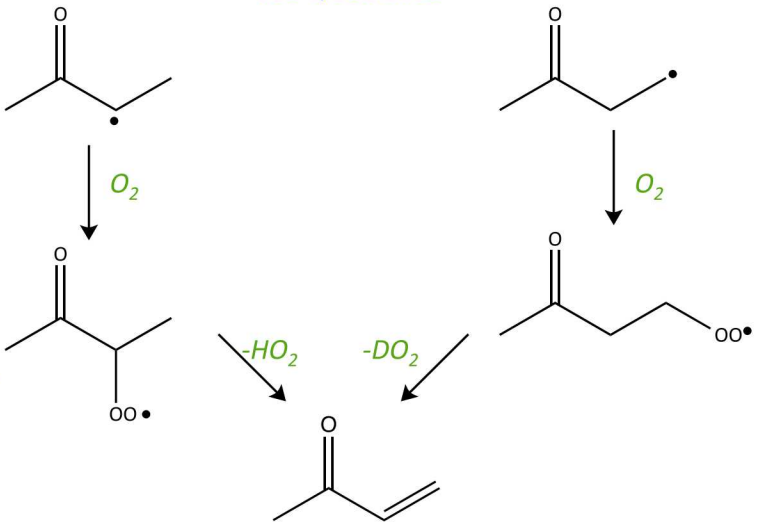




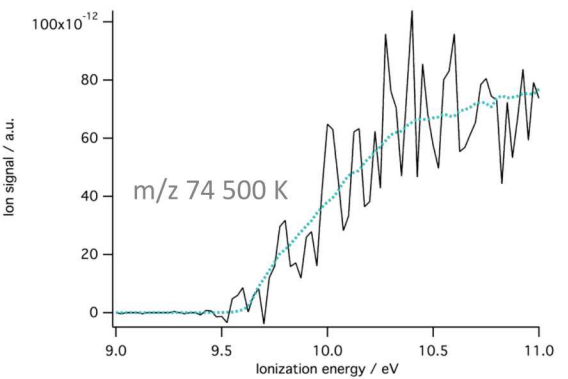


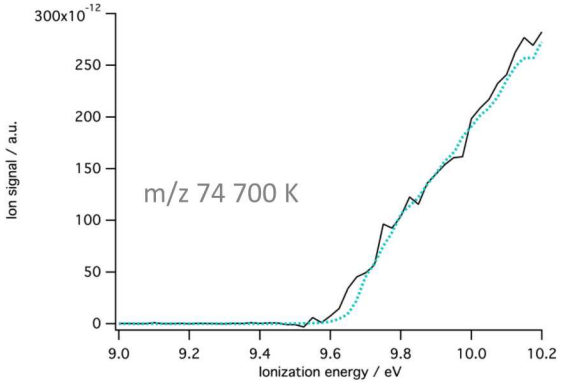


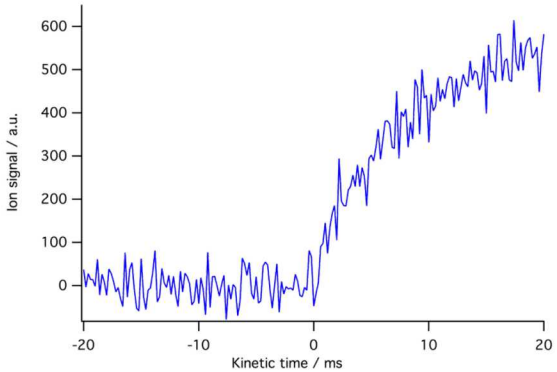
700 K/500 K: 10

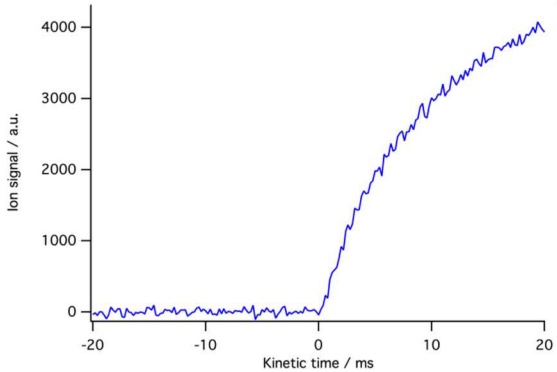


Methyl vinyl ketone

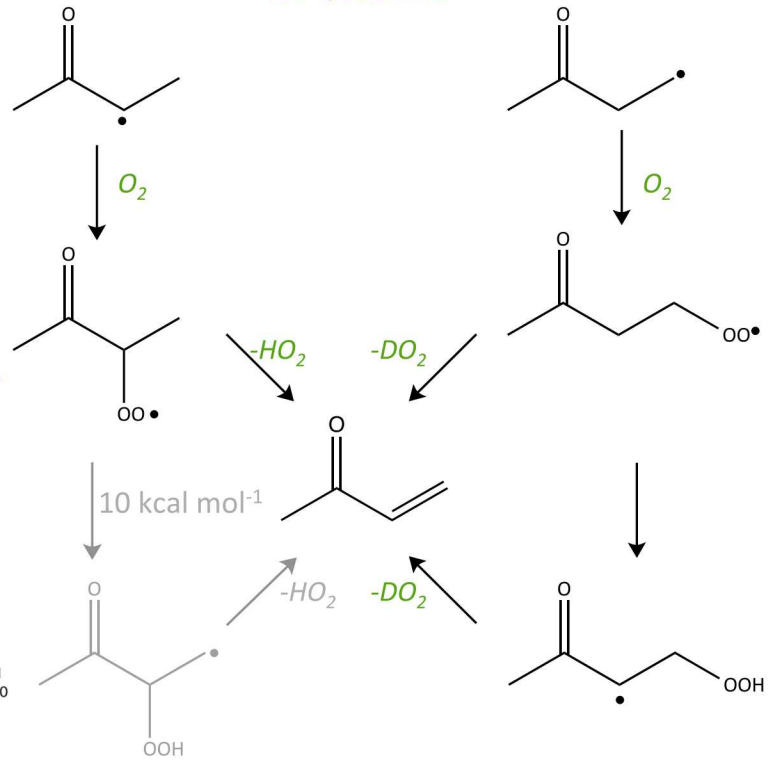




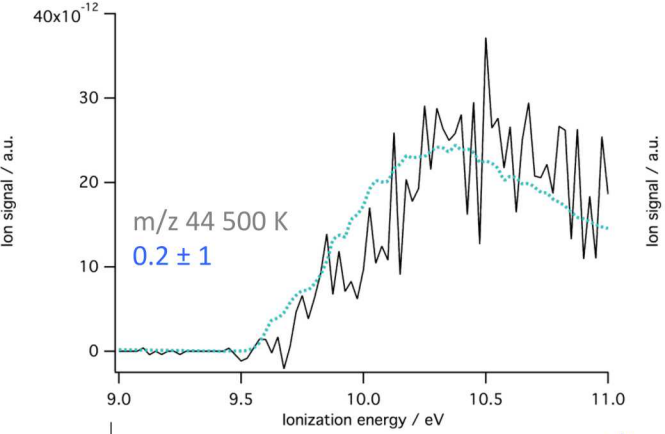


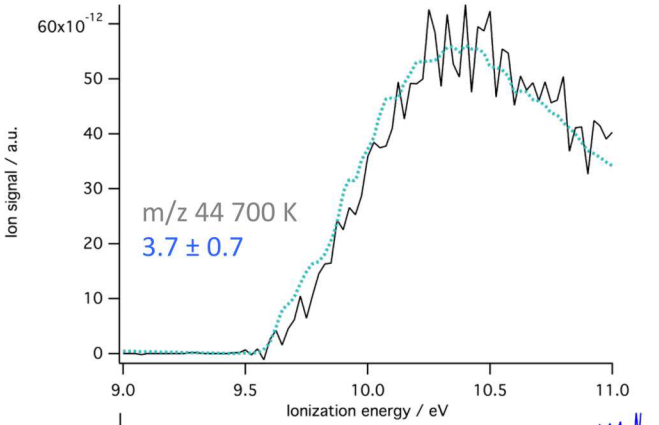


700 K/500 K: 10

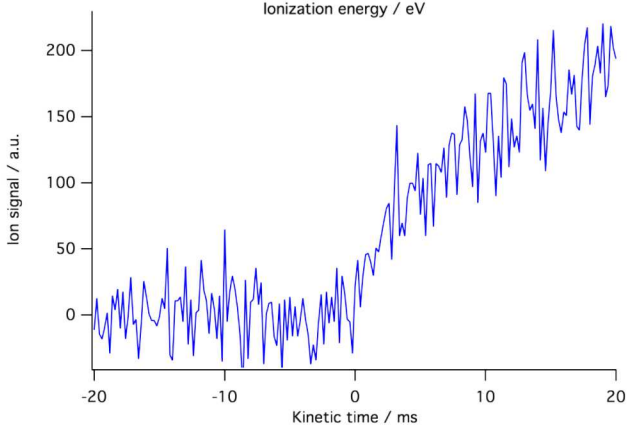


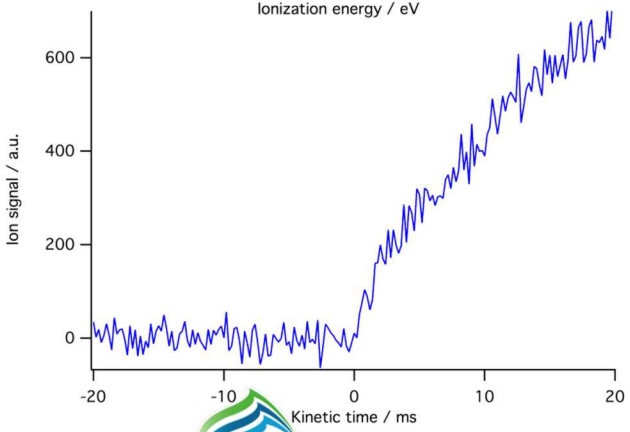
Ketene



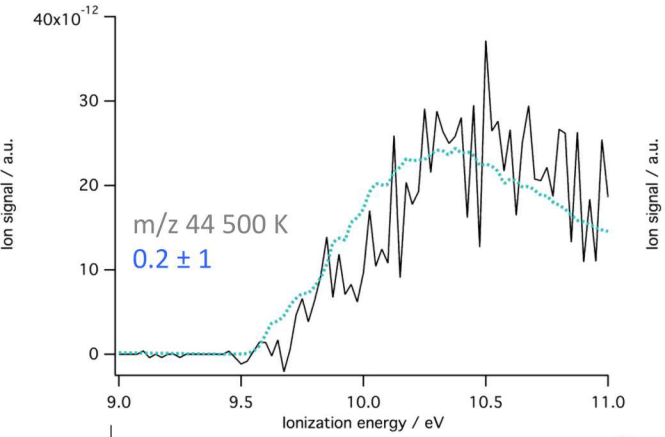


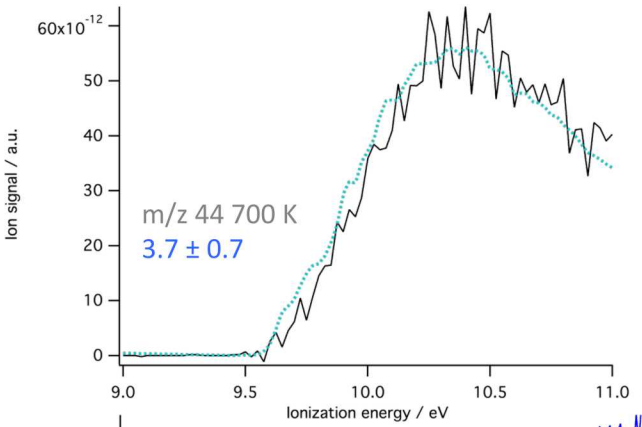
700 K/500 K: 3.7

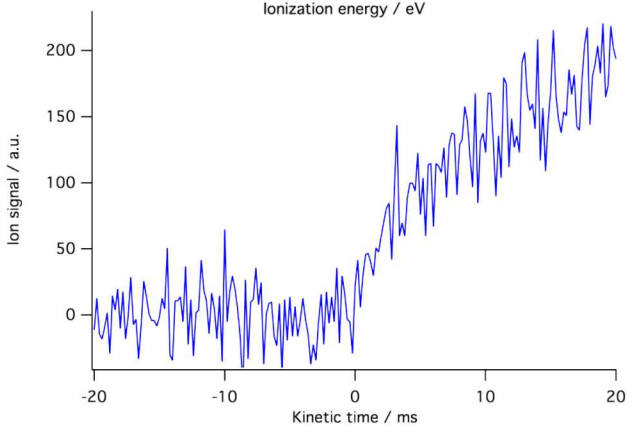


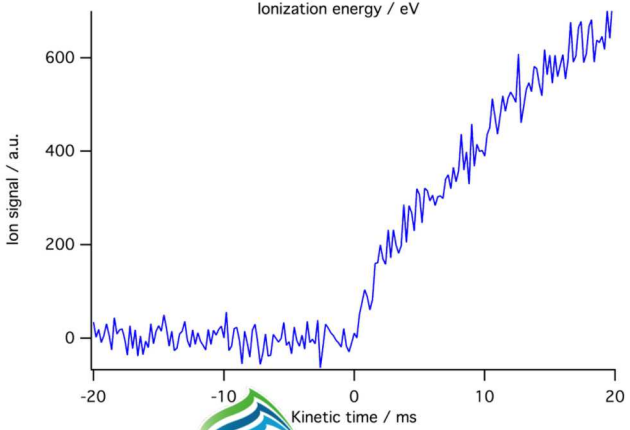


Ketene

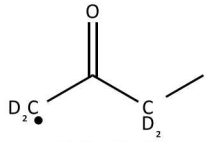






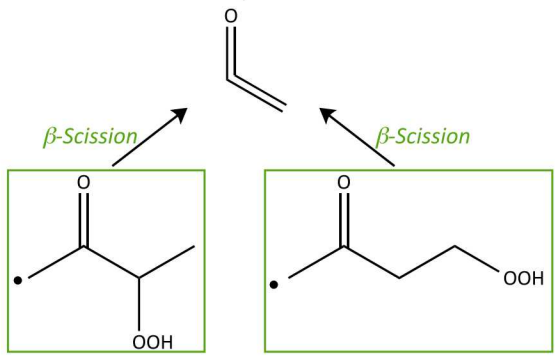


700 K/500 K: 3.7

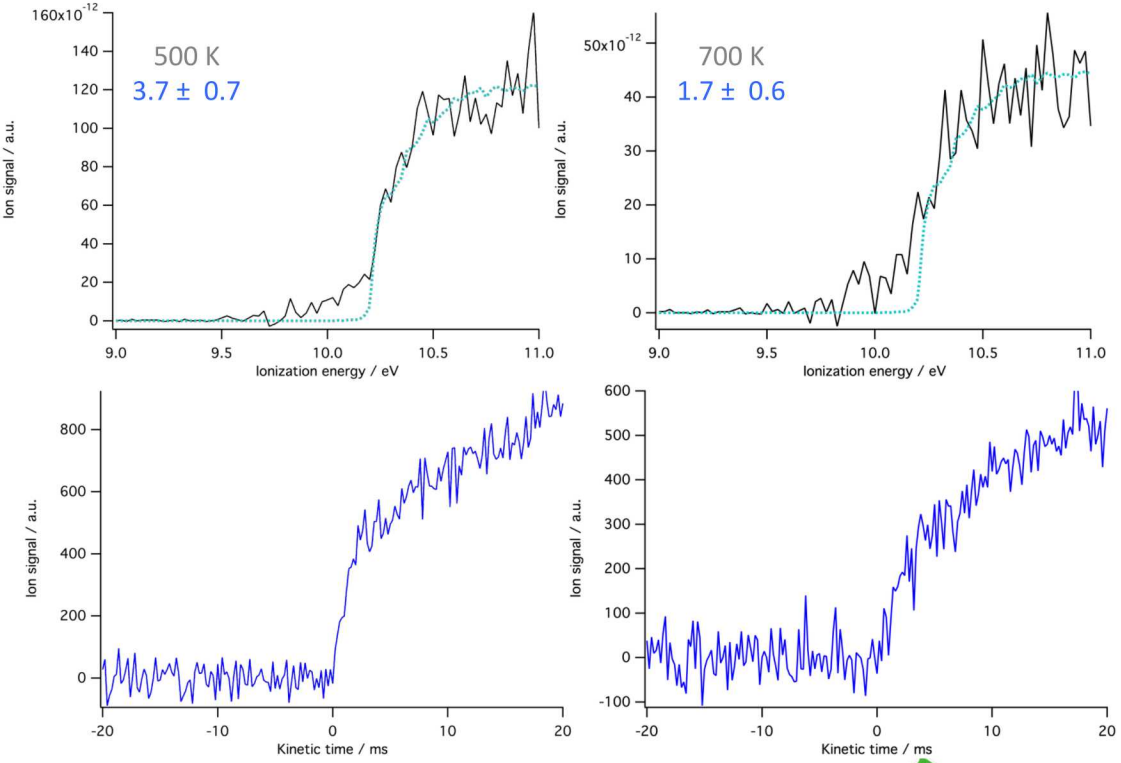


R1: 3 %

β-Scission

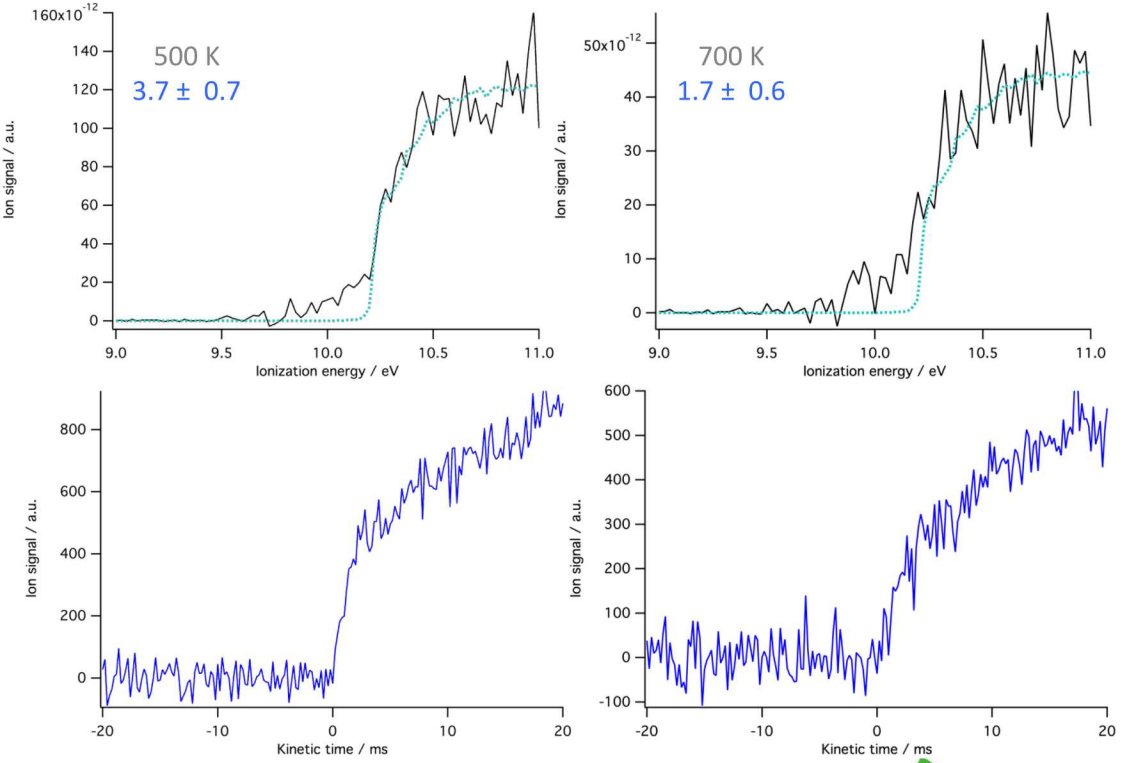


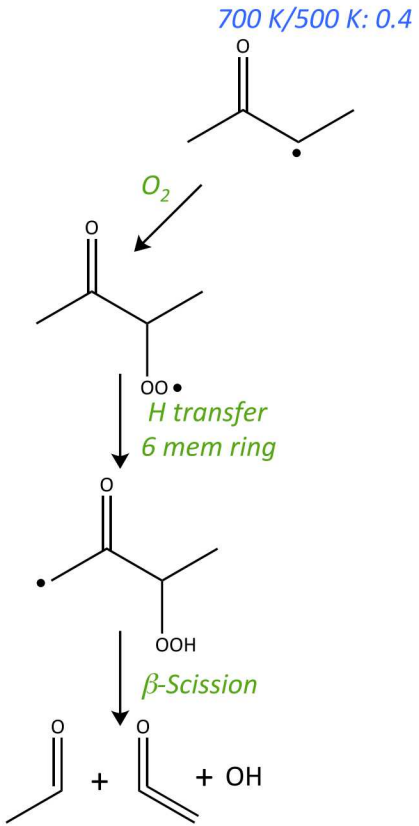
Acetaldehyde



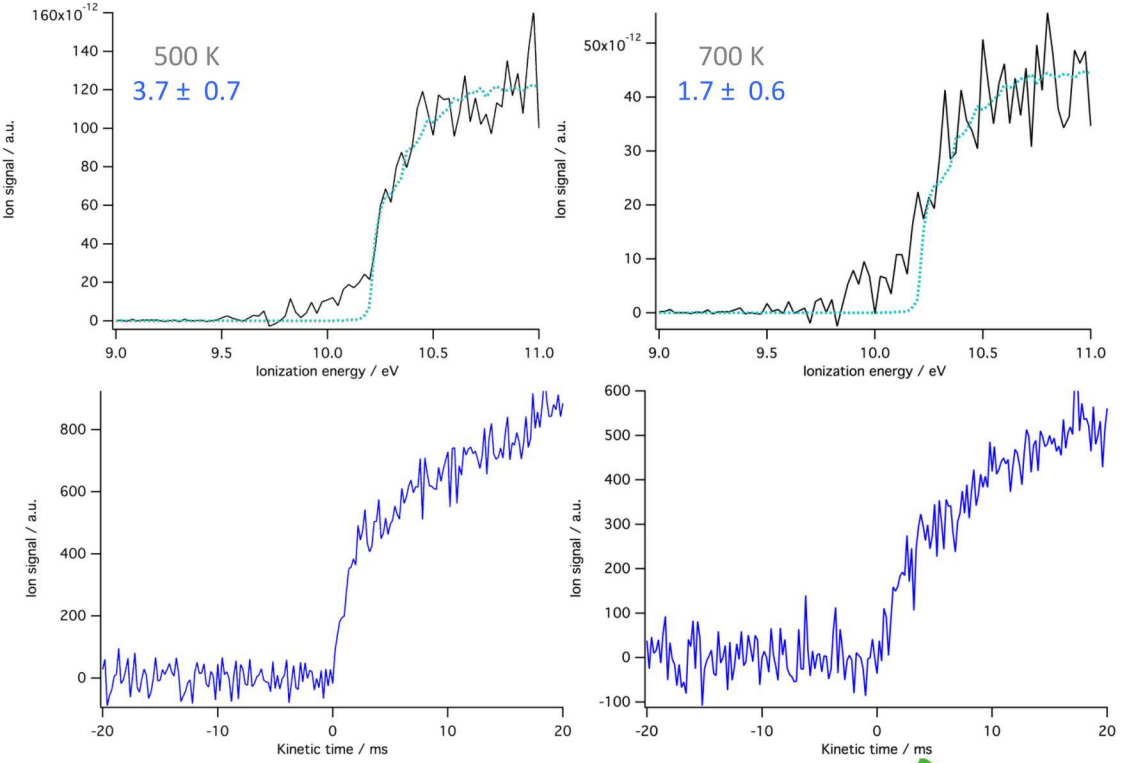
700 K/500 K: 0.4

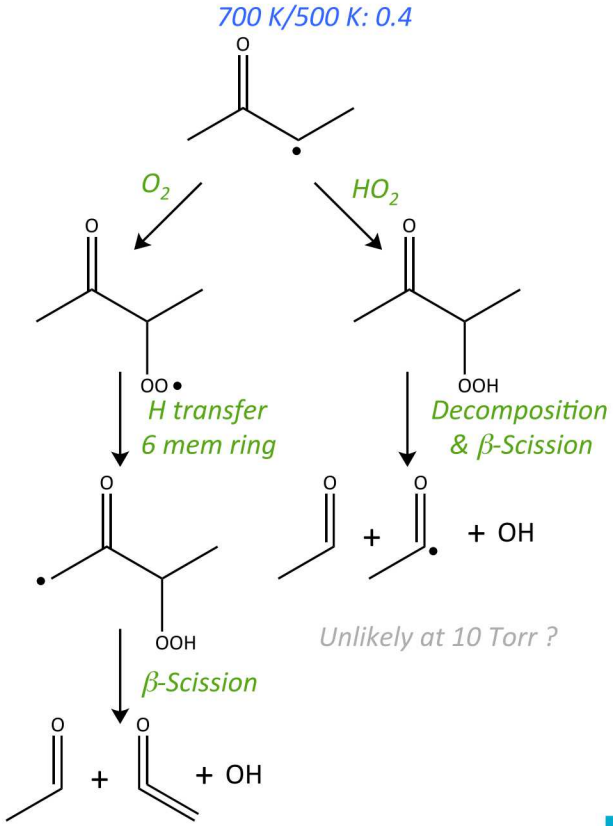
Acetaldehyde



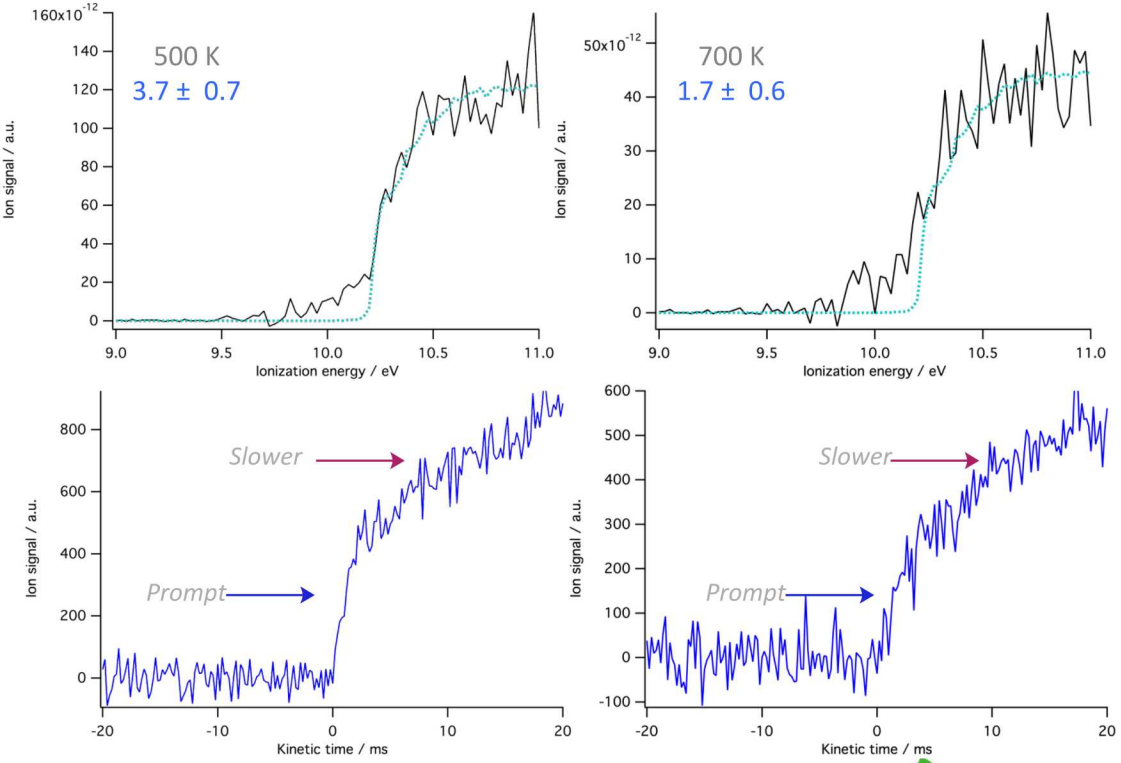


Acetaldehyde



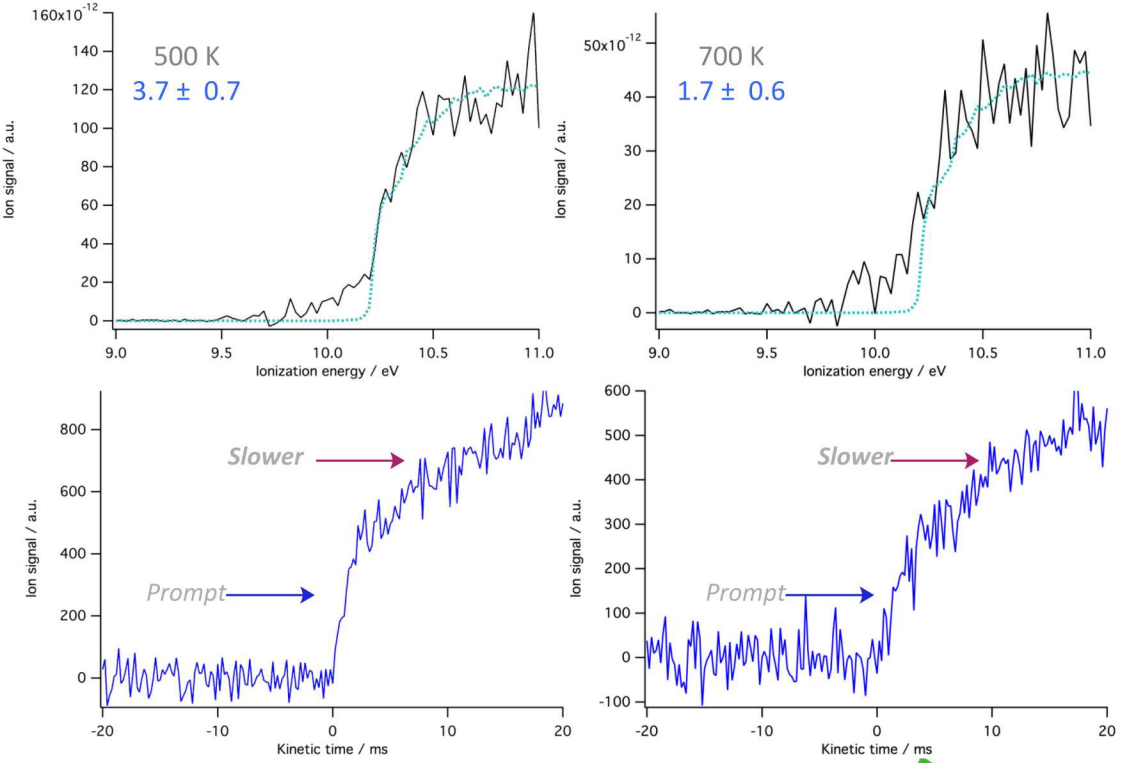


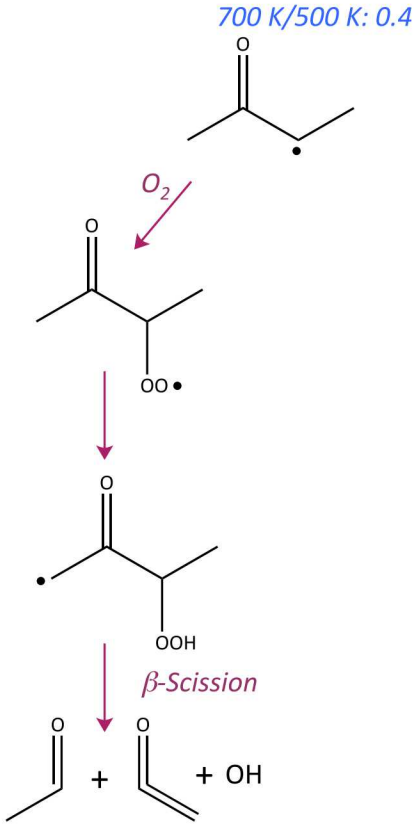
Acetaldehyde



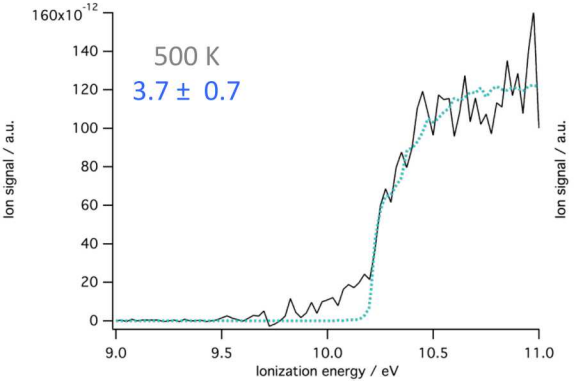
700 K/500 K: 0.4

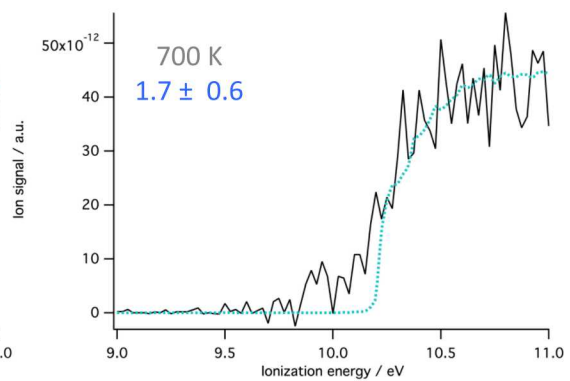
Acetaldehyde

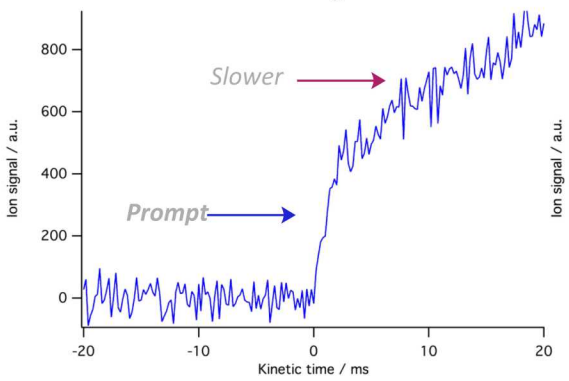


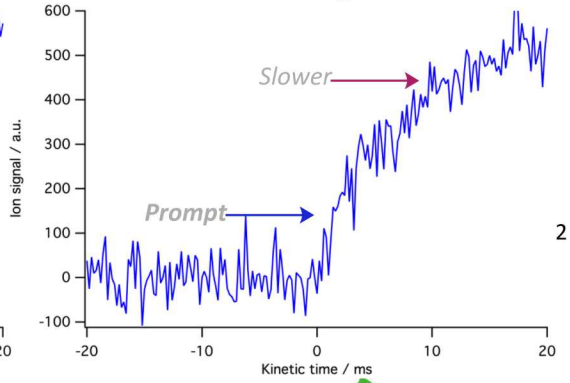


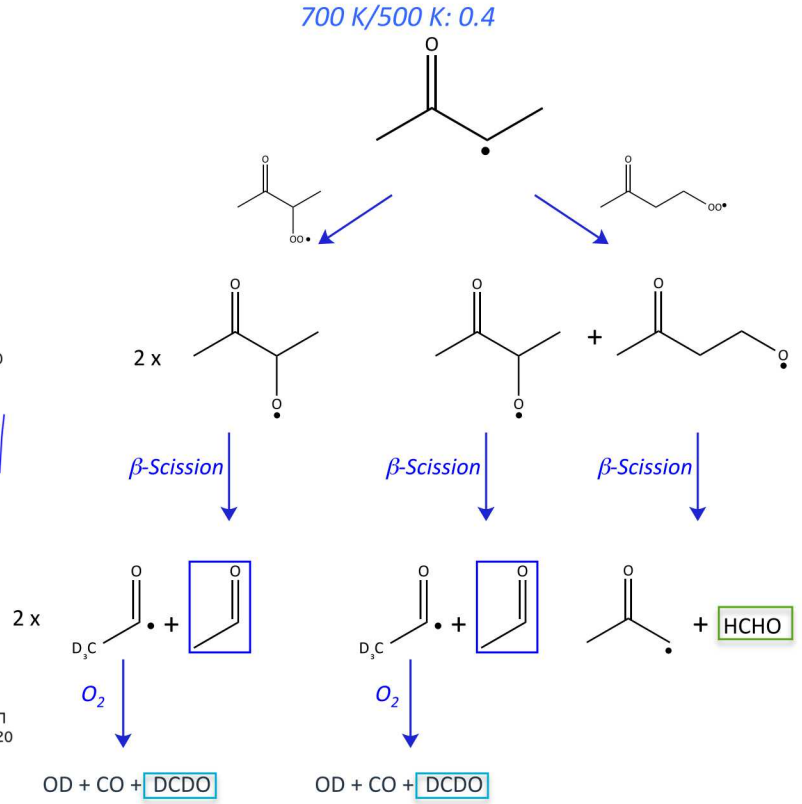
Acetaldehyde



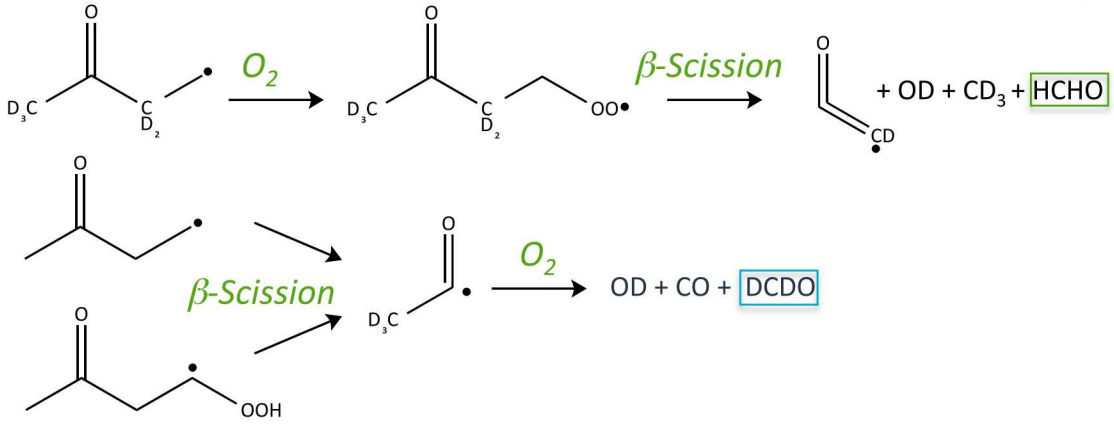






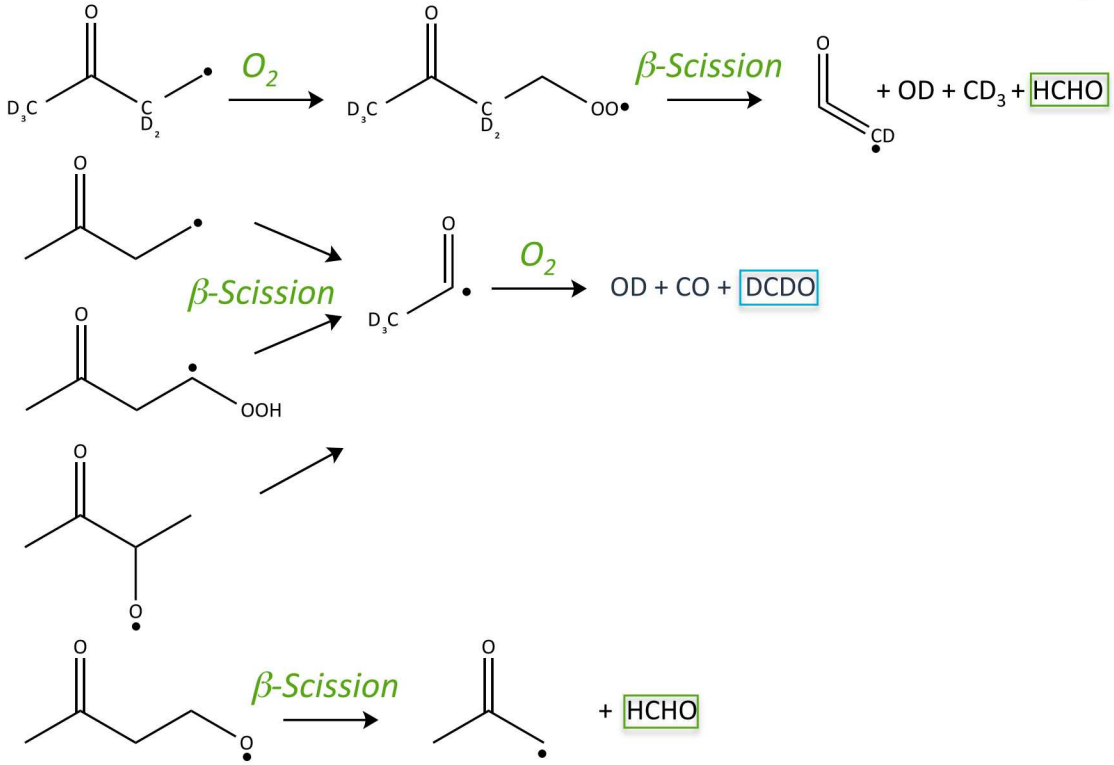


Formaldehyde



S J.. Carr *et al.*, *J. Phys. Chem. A*, **2011**, *115* (6),1069–1085
M. T. B. Romero *et al.*, *Faraday Discuss.*, **2005**, *130*, 73-88
N. I. Butkovskaya *et al.*, *J. Phys. Chem. A*, **2004**, *108*, 1160–1168.

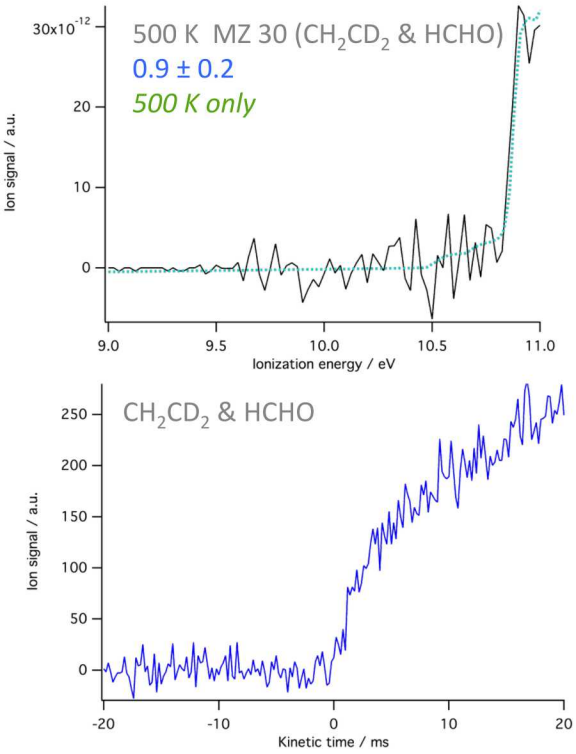
Formaldehyde

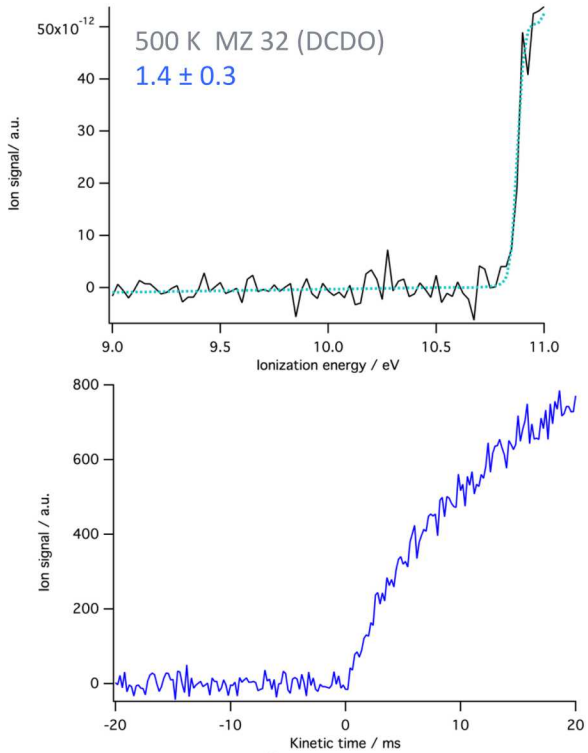


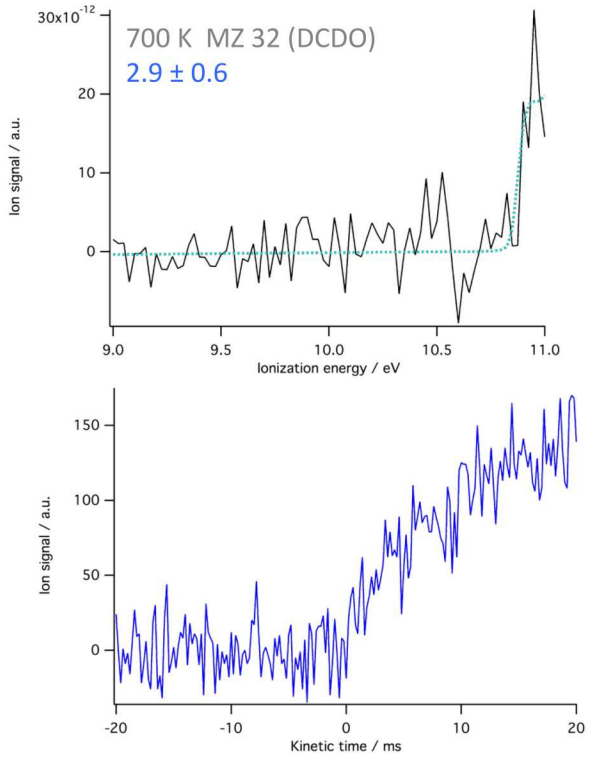
S J.. Carr *et al.*, *J. Phys. Chem. A*, **2011**, *115* (6),1069–1085
M. T. B. Romero *et al.*, *Faraday Discuss.*, **2005**, *130*, 73-88
N. I. Butkovskaya *et al.*, *J. Phys. Chem. A*, **2004**, *108*, 1160–1168.

Formaldehyde

700 K/500 K (total): 1.3
700 K/500 K (DCDO): 2.0

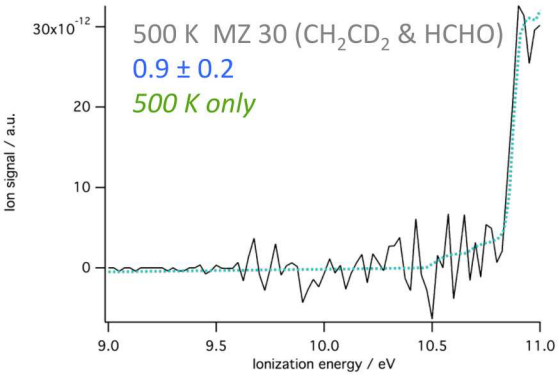


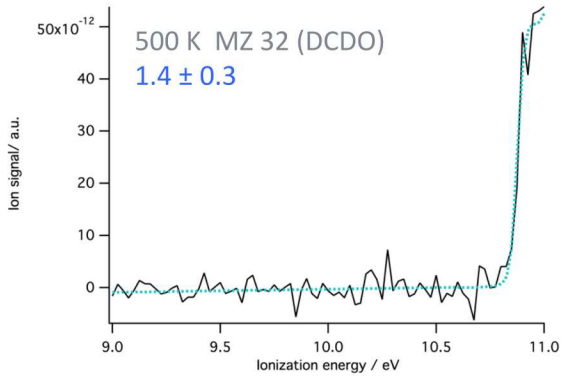


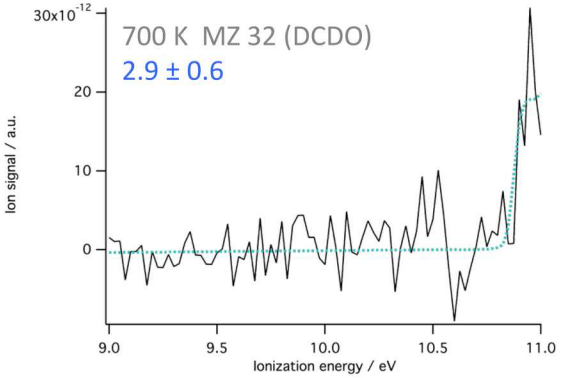


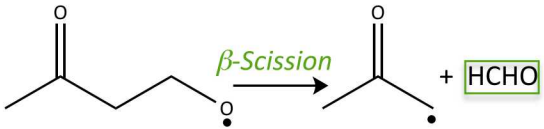
Formaldehyde

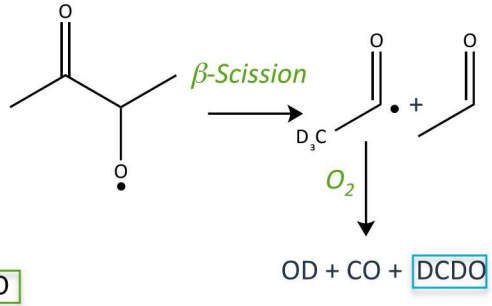
700 K/500 K (total): 1.3
700 K/500 K (DCDO): 2.0

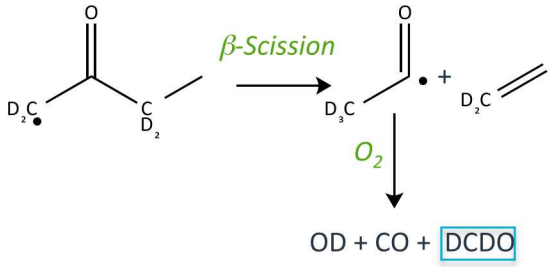


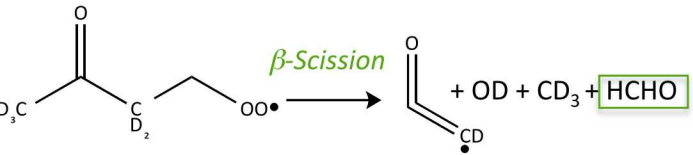






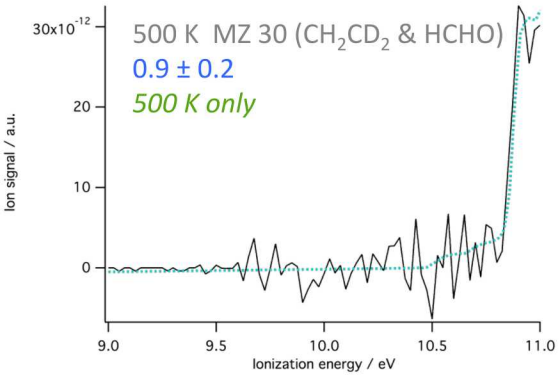


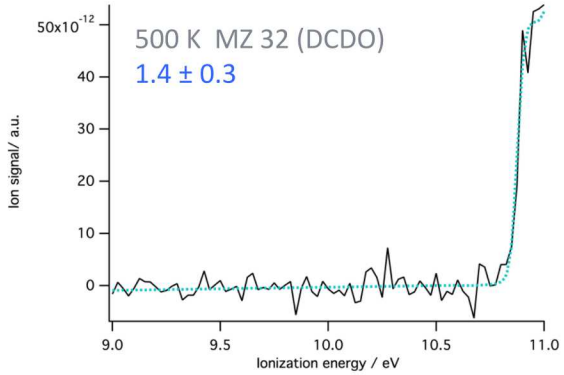


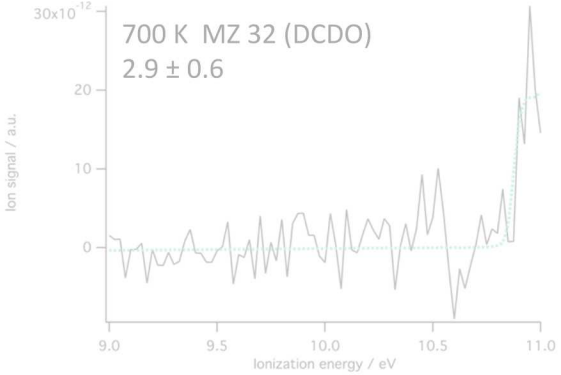


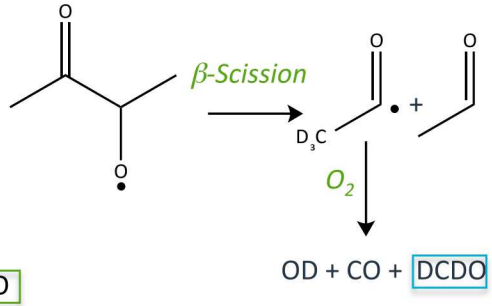
Formaldehyde

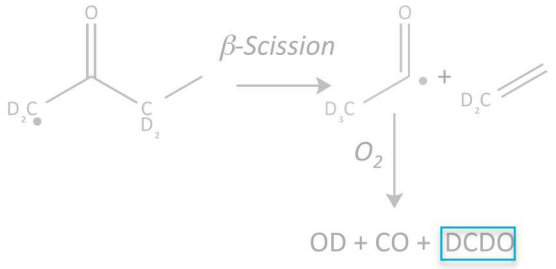
700 K/500 K (total): 1.3
700 K/500 K (DCDO): 2.0





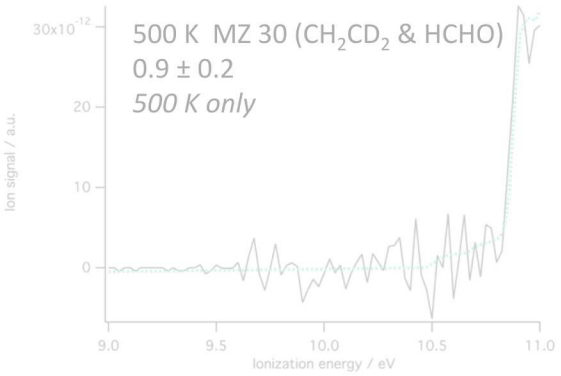


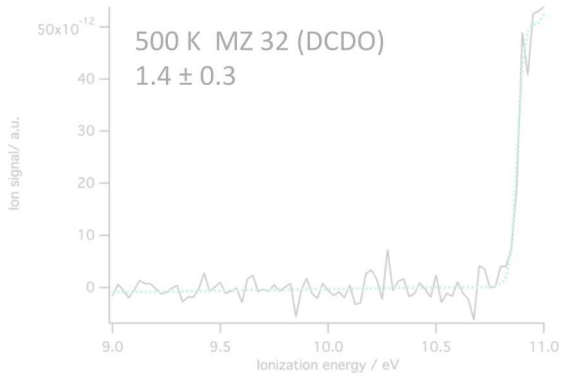


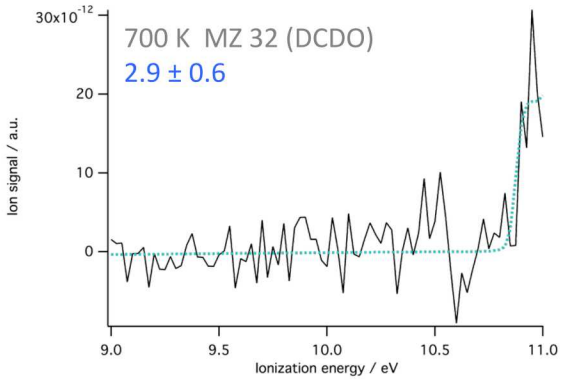


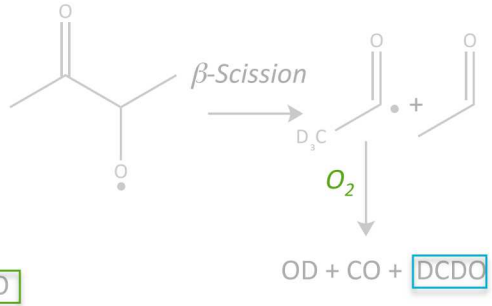
Formaldehyde

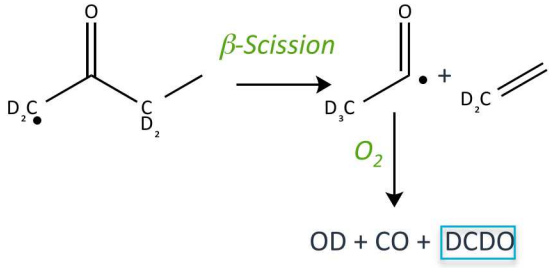
700 K/500 K (total): 1.3
700 K/500 K (DCDO): 2.0



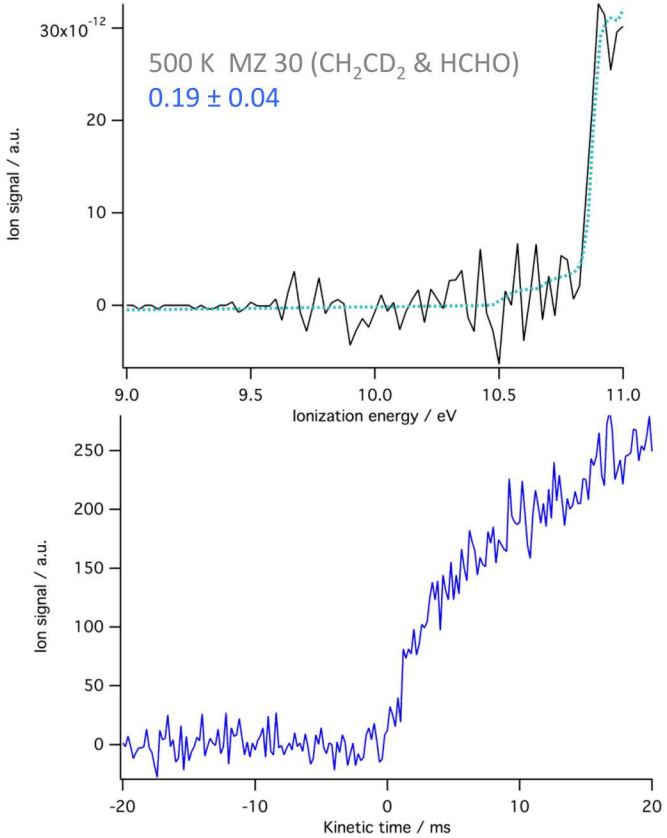


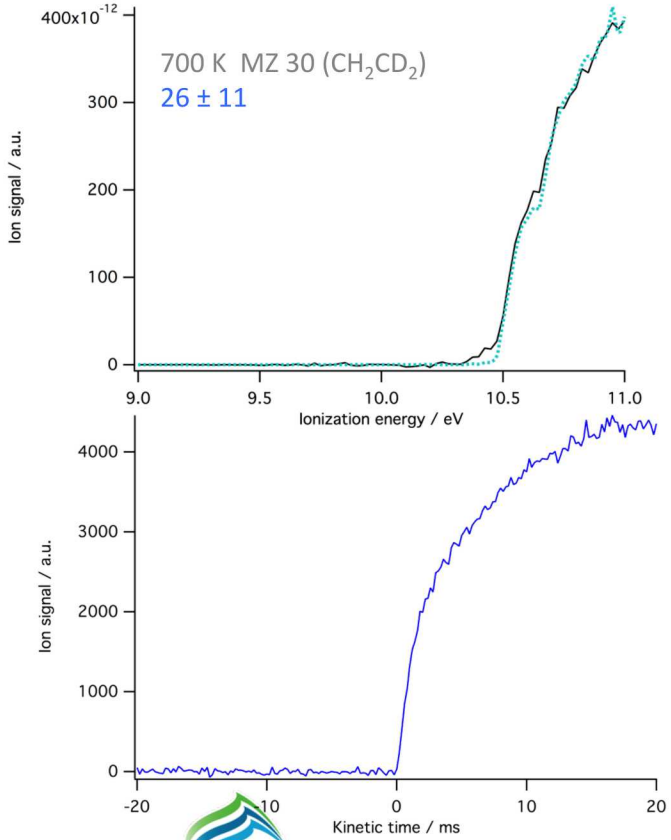






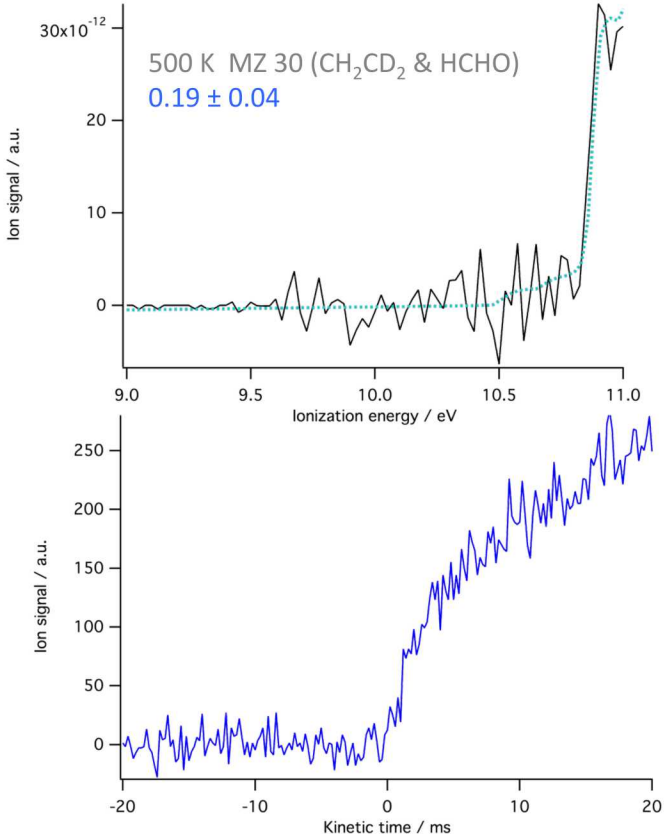
Ethene

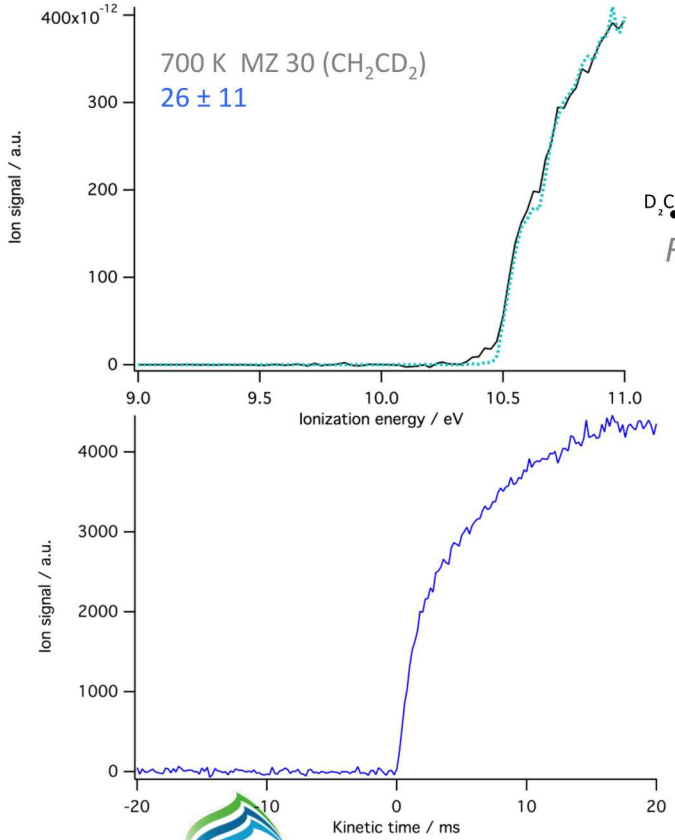


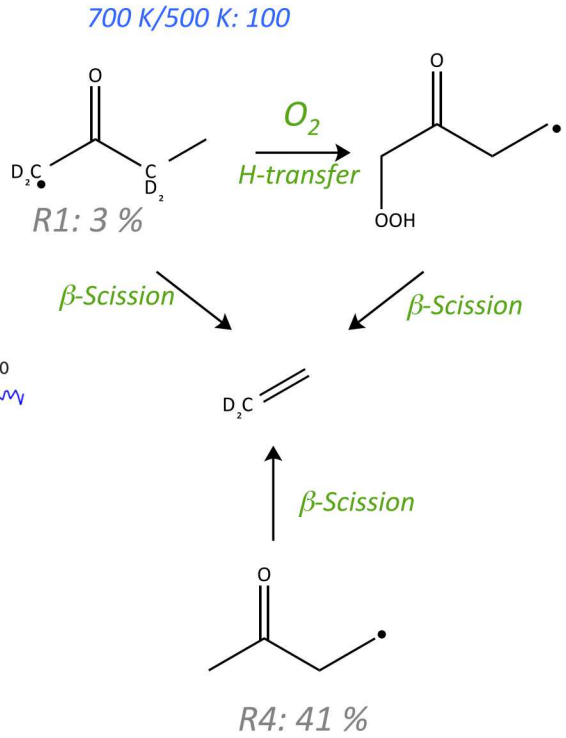


700 K/500 K: 100

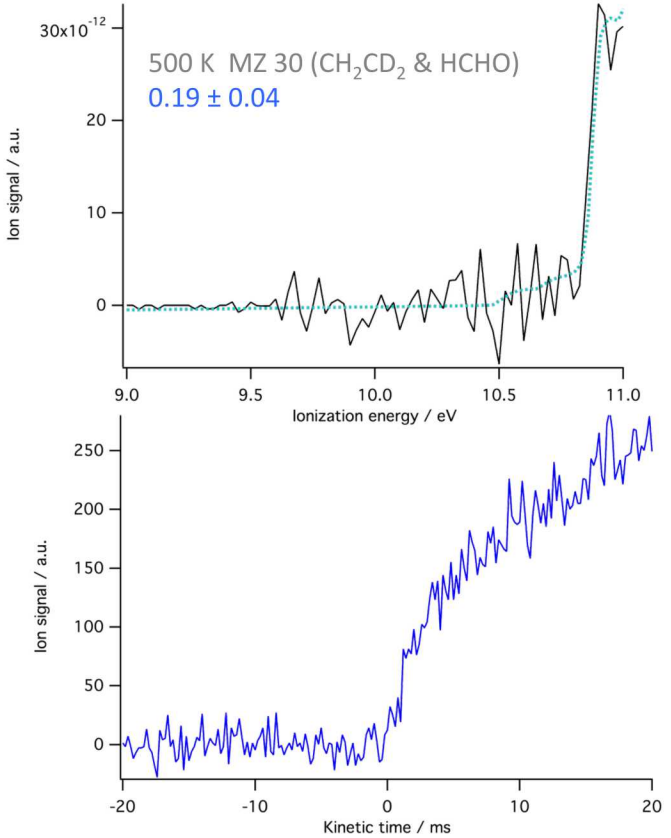
Ethene

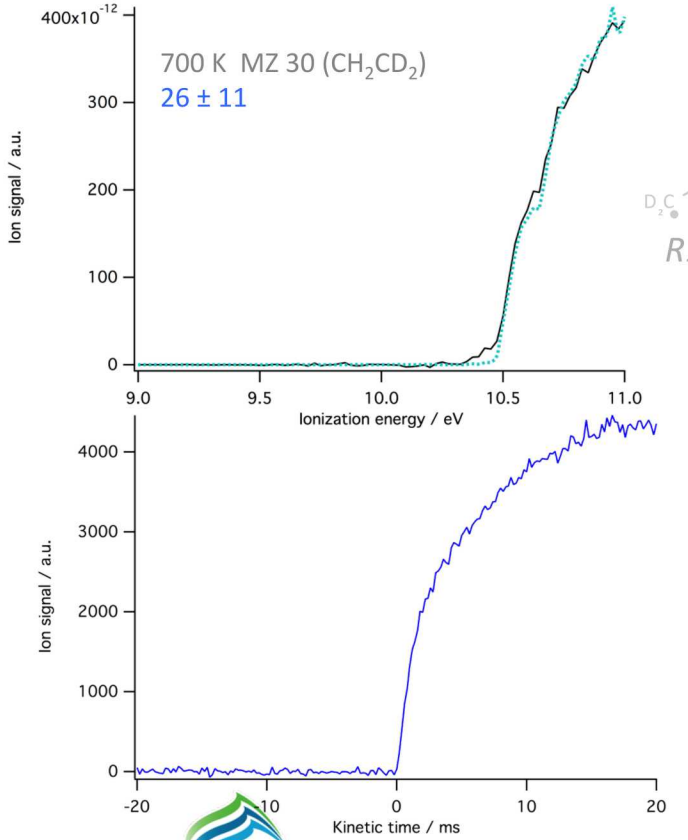

30x10^-12
500 K MZ 30 (CH2CD2 & HCHO)
0.19 ± 0.04
Ion signal / a.u.
Ionization energy / eV
Ion signal / a.u.
Kinetic time / ms

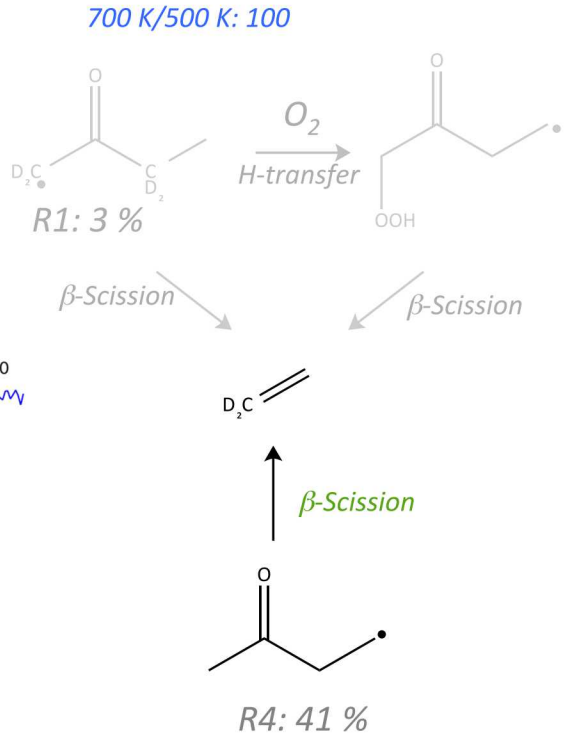

400x10^-12
700 K MZ 30 (CH2CD2)
26 ± 11
Ion signal / a.u.
Ionization energy / eV
Ion signal / a.u.
Kinetic time / ms


700 K/500 K: 100
O2
H-transfer
R1: 3 %
OOH
β-Scission
β-Scission
β-Scission
R4: 41 %

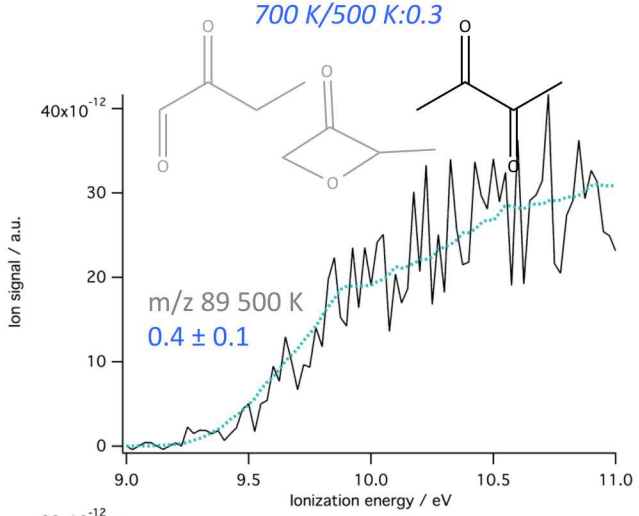
Ethene

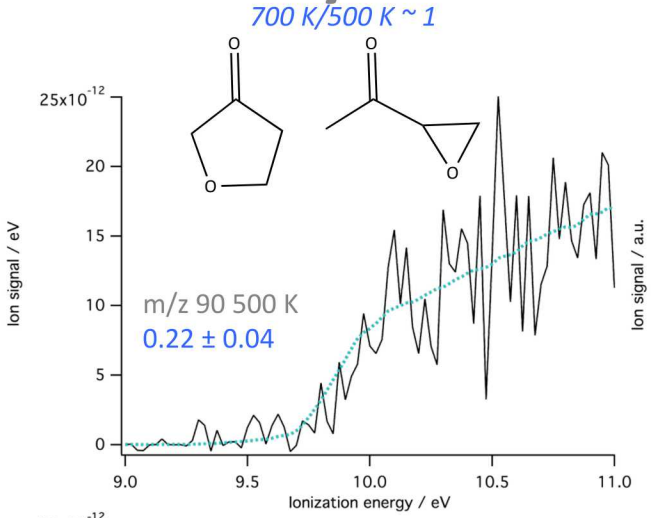

30x10^-12
500 K MZ 30 (CH2CD2 & HCHO)
0.19 ± 0.04
Ion signal / a.u.
Ionization energy / eV
Ion signal / a.u.
Kinetic time / ms

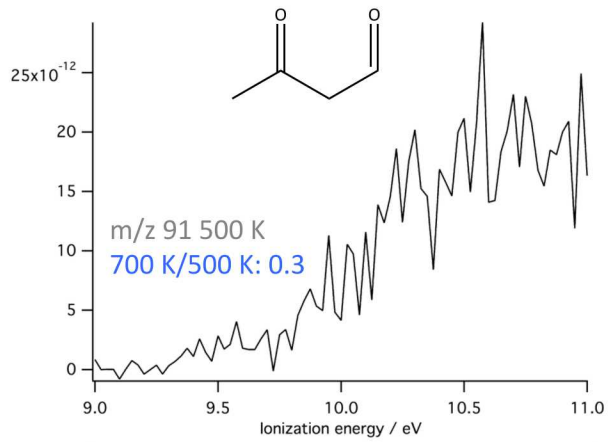

400x10^-12
700 K MZ 30 (CH2CD2)
26 ± 11
Ion signal / a.u.
Ionization energy / eV
Ion signal / a.u.
Kinetic time / ms

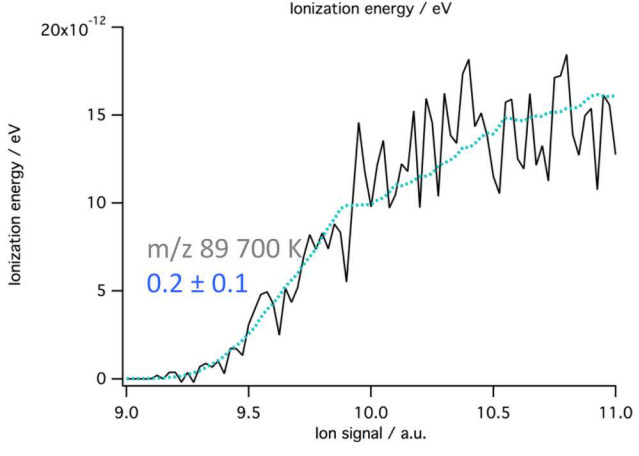

700 K/500 K: 100
O2
H-transfer
R1: 3 %
β-Scission
β-Scission
β-Scission
R4: 41 %

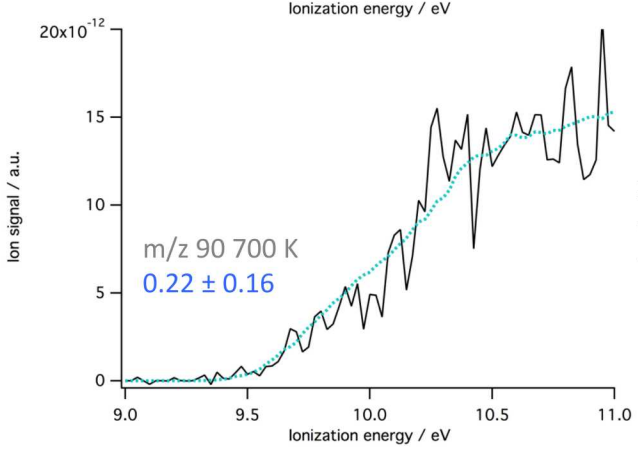
Parent + 14: O-heterocycles and di-carbonyls

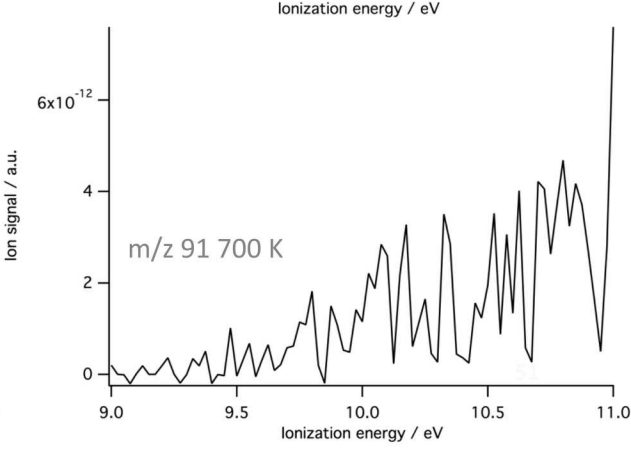




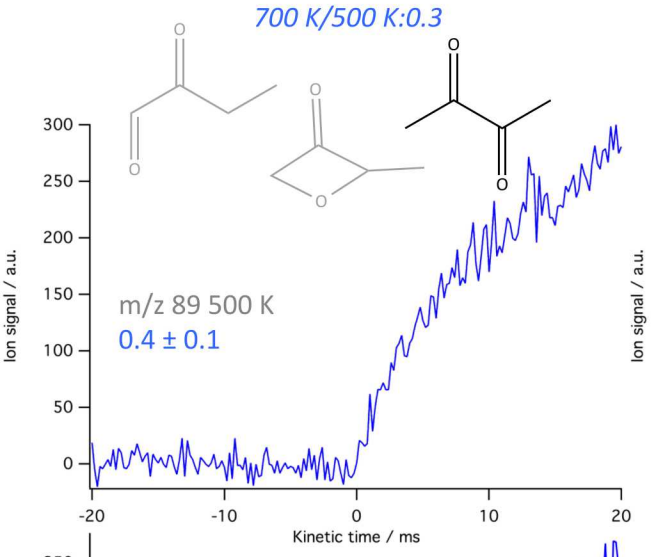


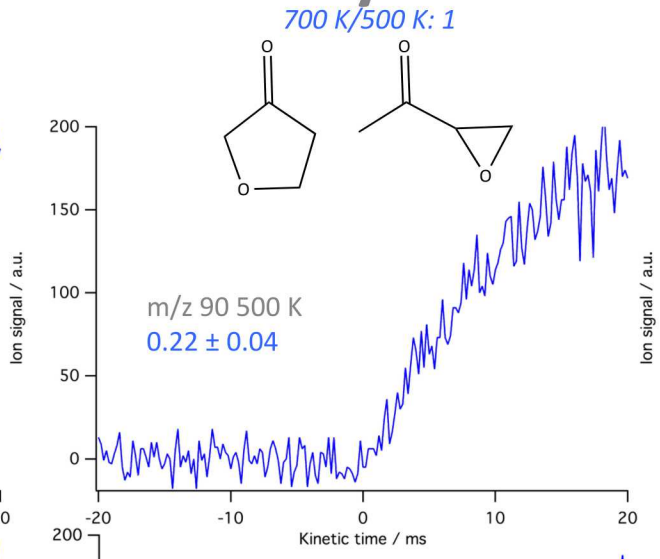


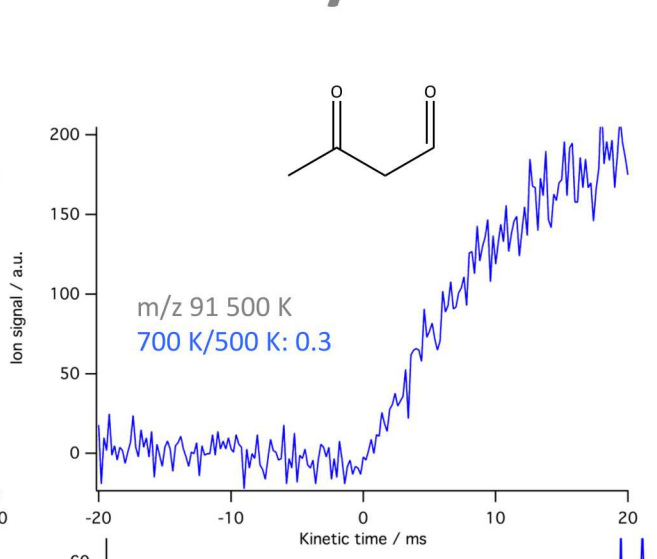


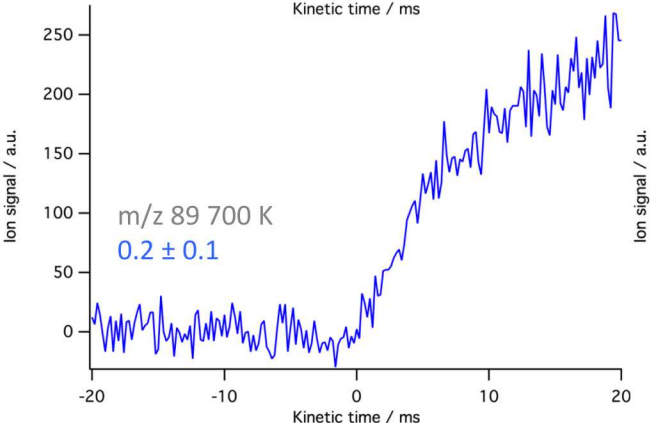


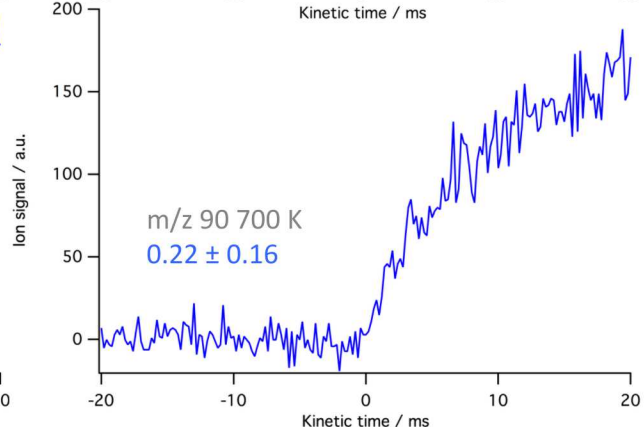
Parent + 14: O-heterocycles and di-carbonyls

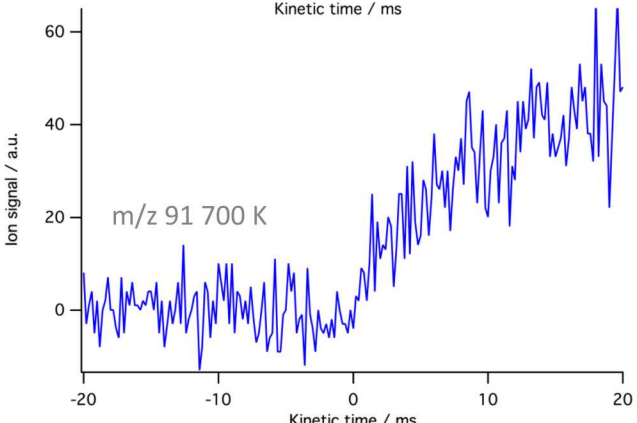


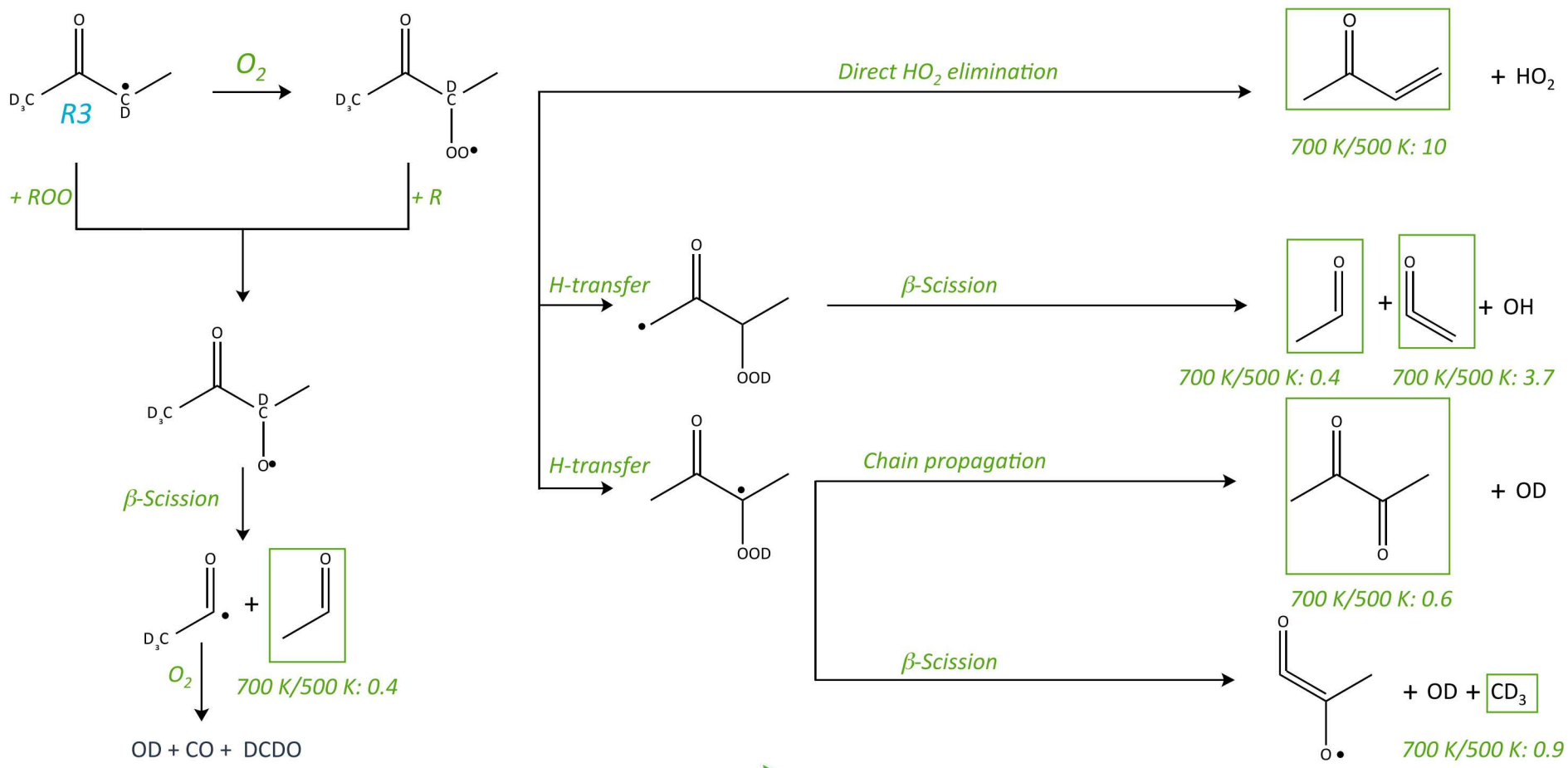


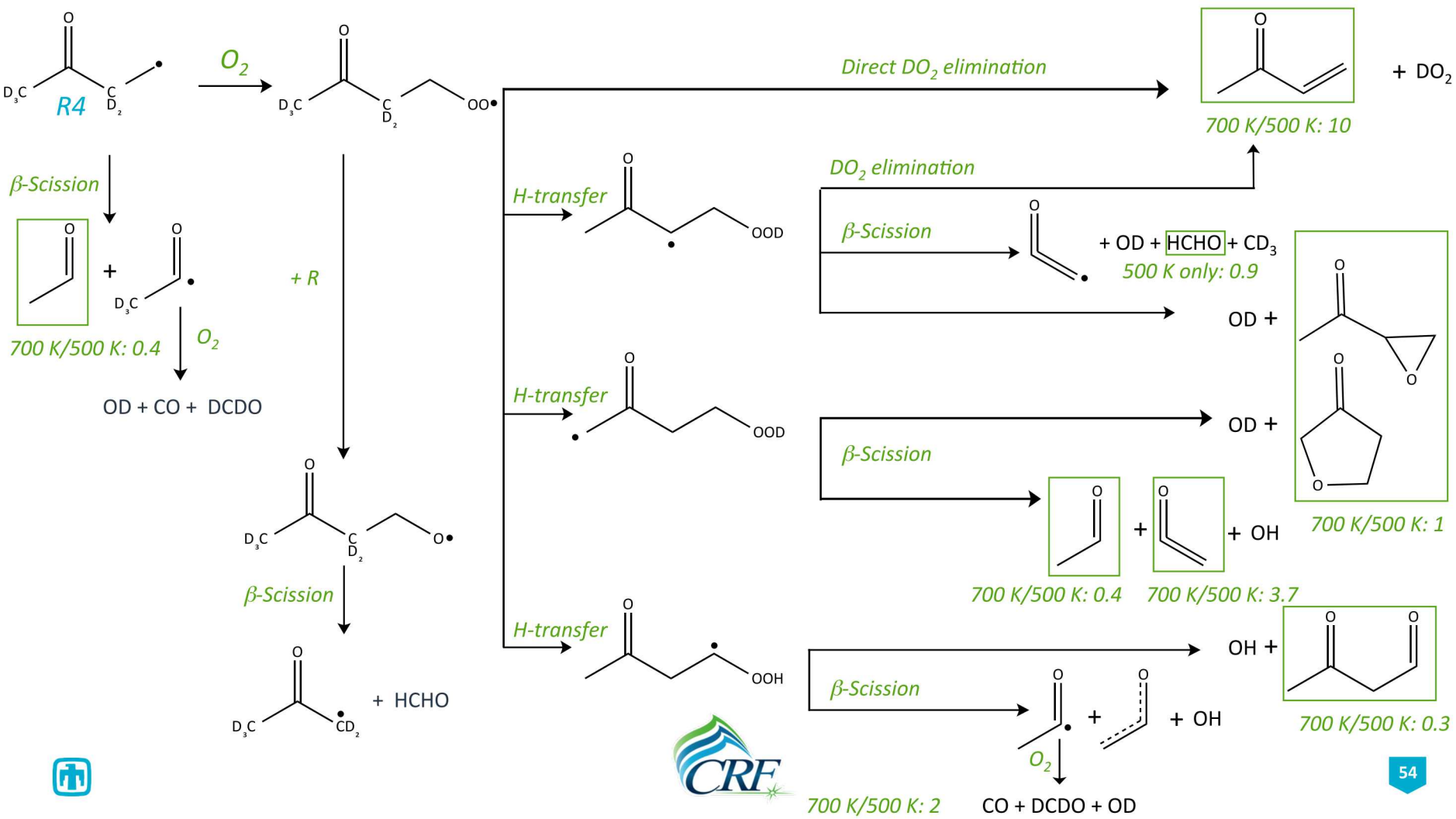









R3
O_2
+ ROO
+ R
β-Scission
O_2
700 K/500 K: 0.4
OD + CO + DCDO
Direct HO_2 elimination
+ HO_2
700 K/500 K: 10
H-transfer
β-Scission
OOD
+ OH
700 K/500 K: 0.4
700 K/500 K: 3.7
H-transfer
Chain propagation
OOD
+ OD
700 K/500 K: 0.6
β-Scission
+ OD + CD_3
700 K/500 K: 0.9


R4
O_2
Direct DO_2 elimination
+ DO_2
700 K/500 K: 10
β-Scission
+ R
700 K/500 K: 0.4
O_2
OD + CO + DCDO
H-transfer
OOD
DO_2 elimination
β-Scission
+ OD + HCHO + CD_3
500 K only: 0.9
OD +
700 K/500 K: 1
H-transfer
OOD
OD +
β-Scission
+ OH
700 K/500 K: 0.4
700 K/500 K: 3.7
β-Scission
+ HCHO
H-transfer
OOH
OH +
β-Scission
+ OH
700 K/500 K: 0.3
O_2
700 K/500 K: 2
CO + DCDO + OD

Summary

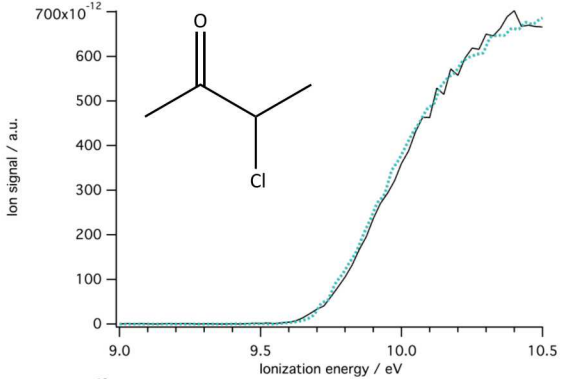
Acknowledgements

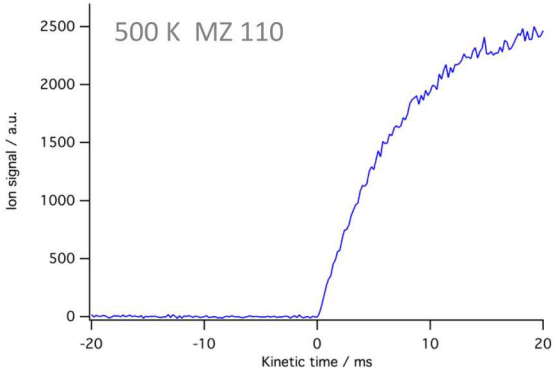
Brandon Rotavera
Krupa Ramasesha
David L Osborn
Craig A Taatjes

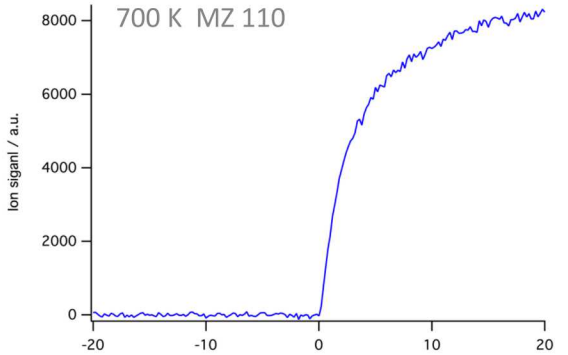
Ewa Papajak
Ivan Antonov
Judit Zádor
Kendrew Au
Lenny Sheps
Ming-Wei Chen
Raybel Almeida

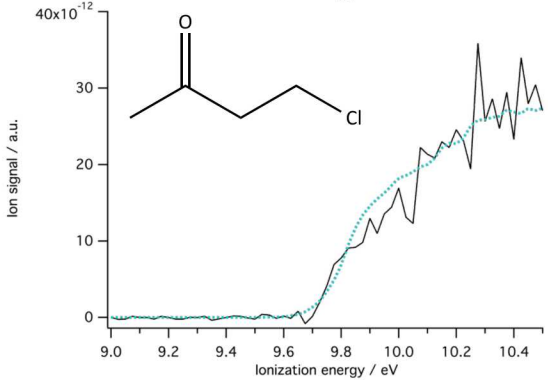
This material is based upon work supported by Office of Chemical Sciences, Biosciences, and Geosciences, Office of Basic Energy Sciences, of the U.S. Department of Energy (BES/USDOE). The Advanced Light Source is supported by the Director, Office of Science, BES/USDOE under Contract DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

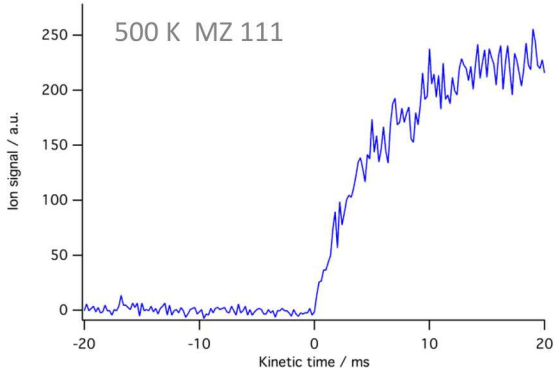
RCl formation

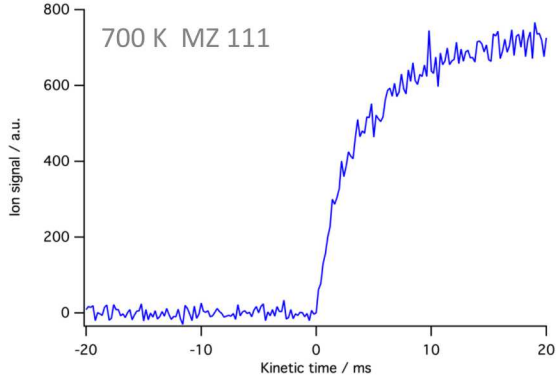




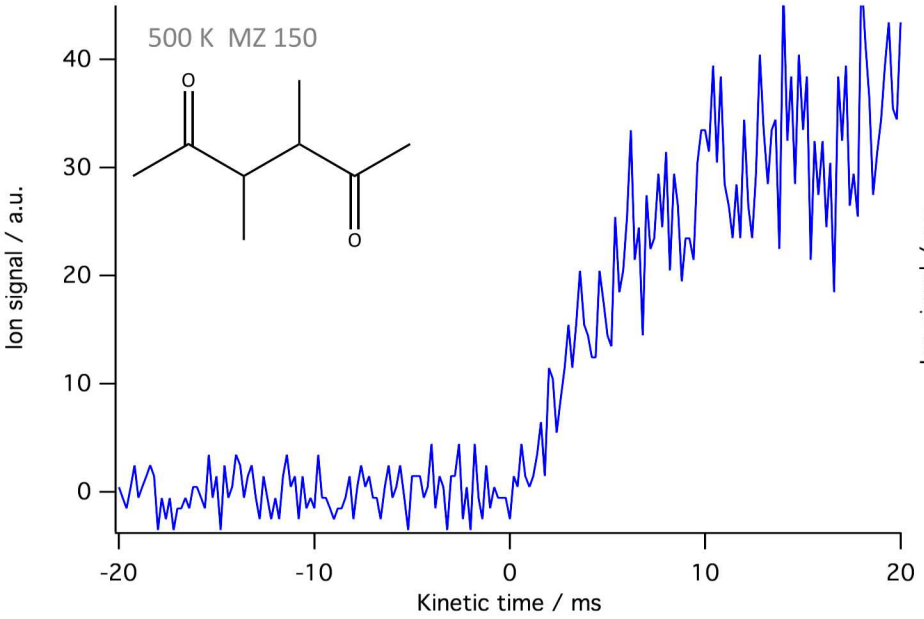


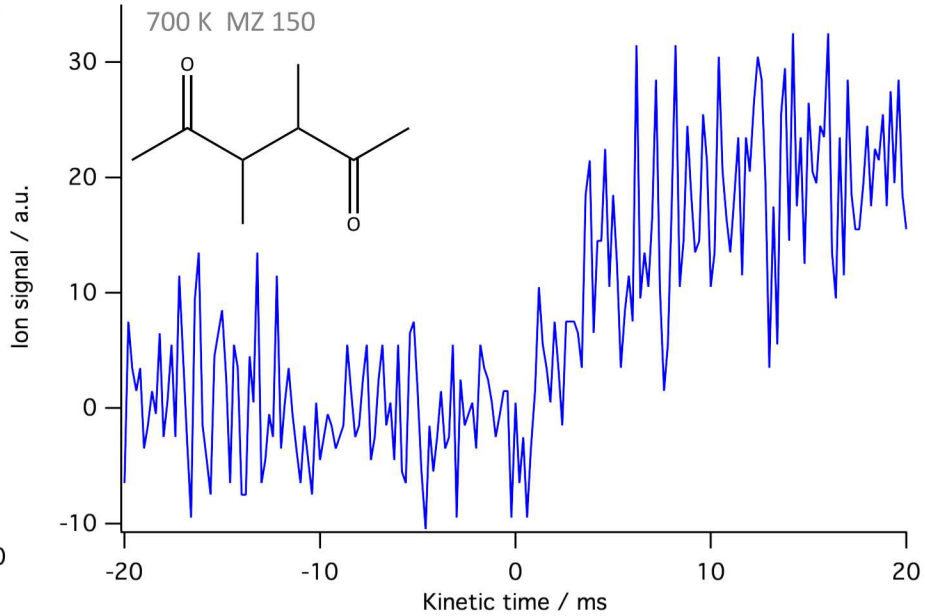






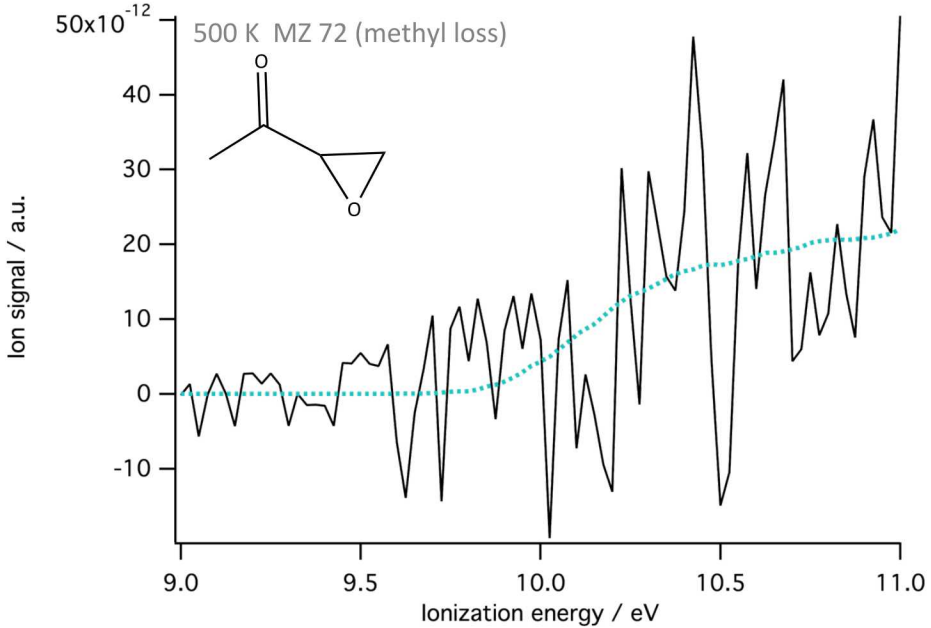
RR dimer formation

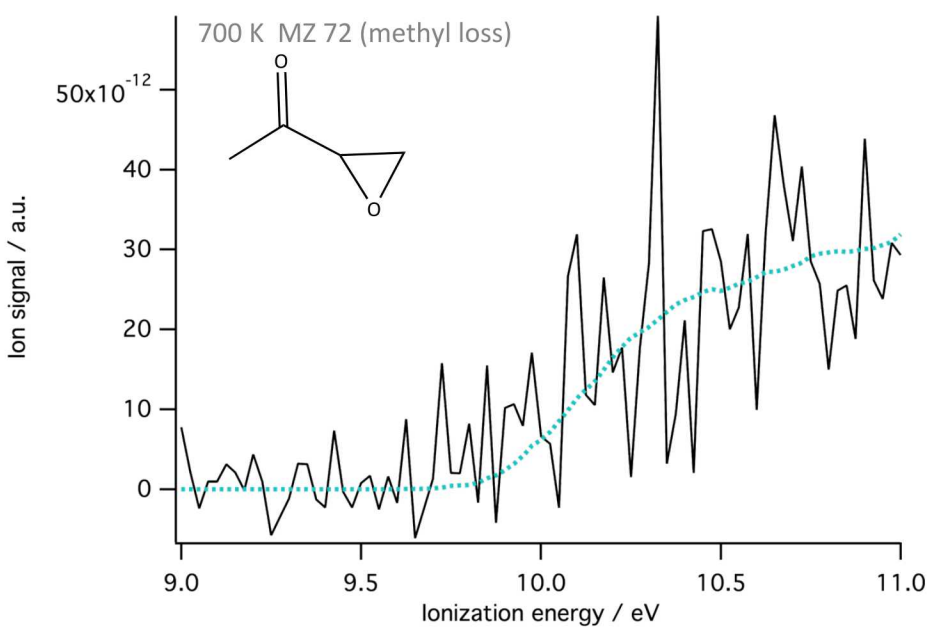


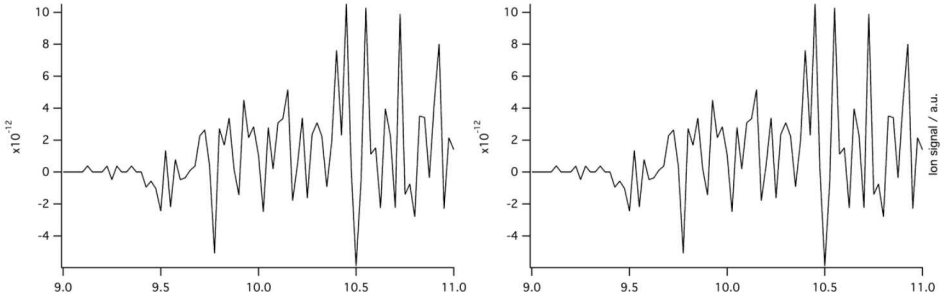


$[O_2]/[Cl]_0$ ratio: Favoring R + O_2 over R + Cl

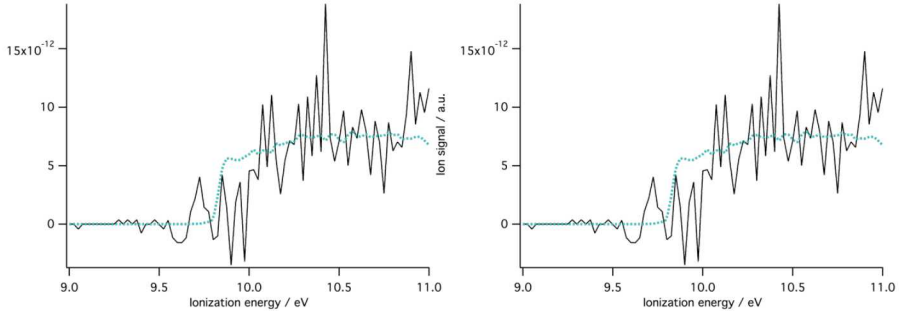
DI from 3-membered ring



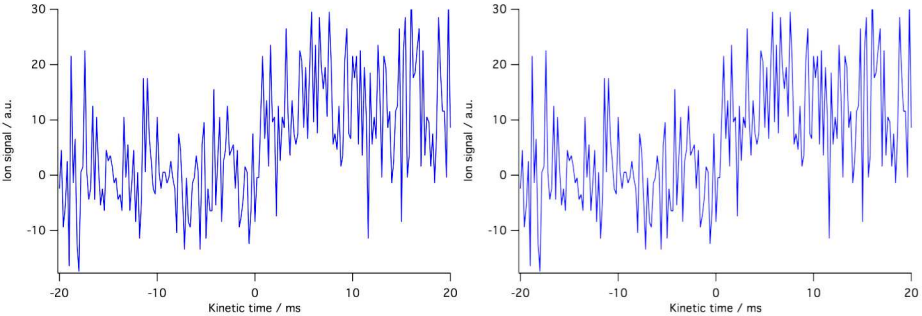


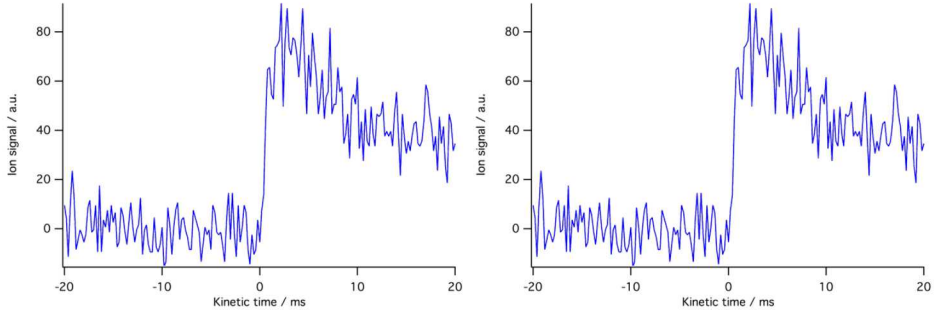


m/z 71: (O)CC(O)CH3 from R3(R3) QOOH scission or (O)CCHCH2O from R3(R4) QOOH scission 500 K & 700 K, D5-butanone



m/z 18 fitted with CH3: from R3(R3) QOOH scission or R3(R4) QOOH scission 500 K & 700 K, D5-butanone





T dependence of OH + butanone R isomers

	rate expression per H	500			700		
alpha CH3	(1.33*(100T^(3.08))exp(475/T))/6.022×10^23	1.24E-13	*3.73E-13*	*10%*	2.63E-13	*7.89E-13*	*15%*
alpha CH2	1.18*(100T^(3.15))exp(1535/T)/6.022×10^23	1.34E-12	*2.68E-12*	*70%*	1.61E-12	*3.22E-12*	*61%*
beta CH3	0.45*(T^(3.81))exp(1459/T)/6.022×10^23	2.65E-13	*7.96E-13*	*21%*	4.15E-13	*1.25E-12*	*24%*
Total rate coefficient			3.85E-12			5.25E-12	

C.-W. Zhou *et al.*,*Phys. Chem. Chem. Phys.*, **2011**, *13*, 11175–11192