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Products of Criegee Intermediate Reactions with NO_2: Experimental Measurements and Tropospheric Implications

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Carl J. Percival, Dudley E. Shallcross & Craig A. Taatjes.

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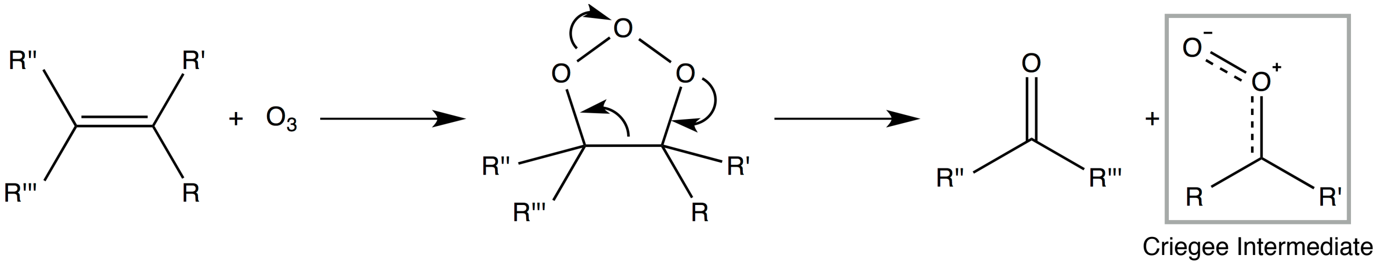
Jet Propulsion Laboratory, Pasadena, CA, USA

Criegee Intermediates

- Criegee intermediates are formed principally from reactions of ozone with alkenes.



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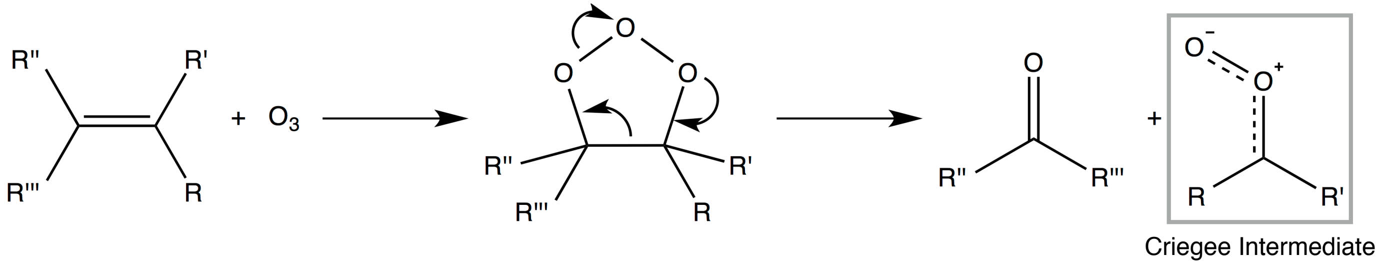
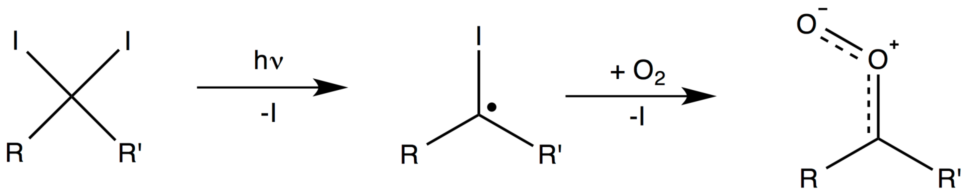


- Advent of photolytic pathways to Criegee intermediate production enables direct kinetic and product studies



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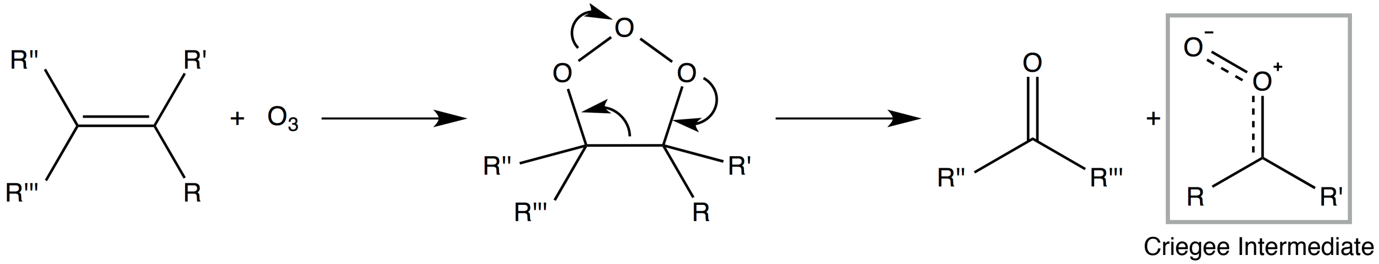

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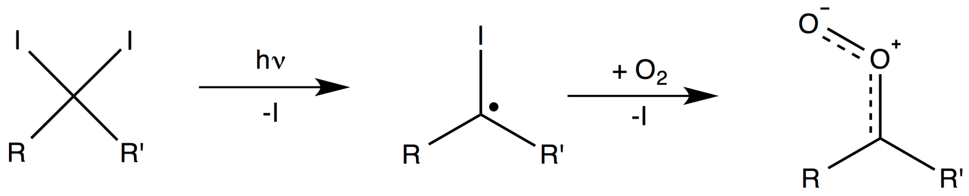

- This method has enabled multitude of studies, and in many cases revealing it to be more reactive than initially predicted.
  - For example the reaction of formaldehyde oxide (3.4×10^{-11} molecule cm^{-3} s^{-1}) with SO_2 is **~ 1000 times faster** than previously thought.

- To fully assess the impact of these reactions in the atmosphere, **the products, as well as the kinetics, need to be understood**.

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The Importance of Criegee + NO_2

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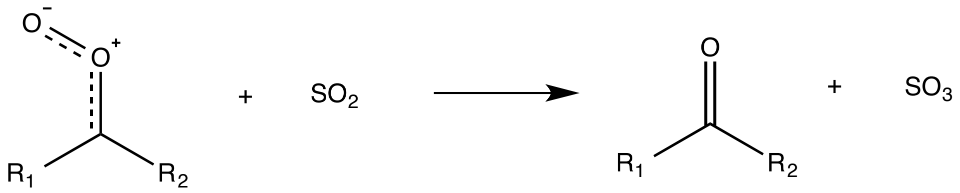

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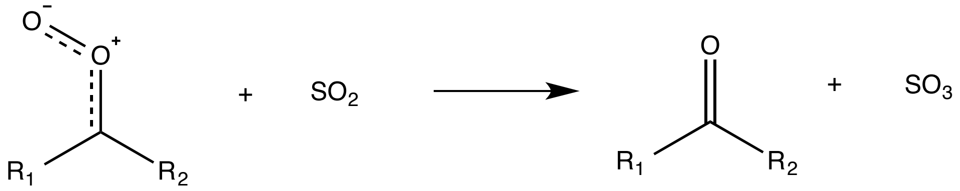
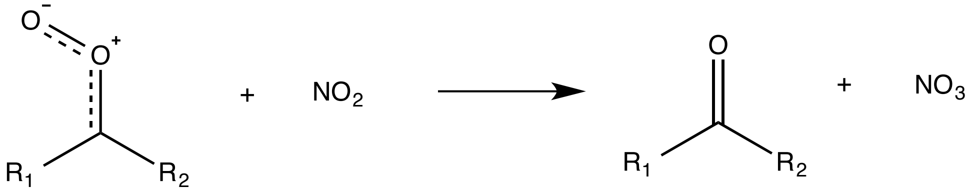


- Previous studies have demonstrated rate coefficient for Criegee intermediate + NO_2 to be rapid (~ 2×10^{-12} molecule cm^{-3} s^{-1}), it has been thought that the reaction products are analogous to those in the reaction with SO_2:



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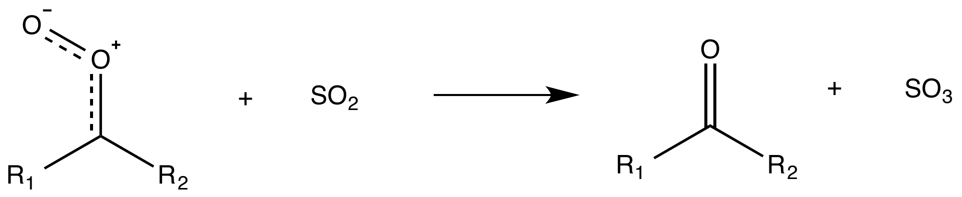

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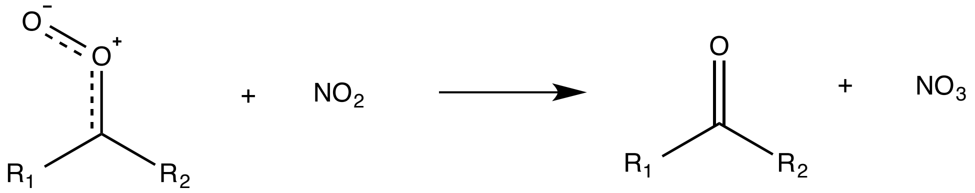

- In urban areas, which are typically rich in ozone, alkenes and NO_x, this reaction could have a significant impact on NO_x/NO_y budget.
  - Vereecken *et al.*, estimated the potential loss of *syn*-acetaldehyde oxide via reaction with NO_2 to be as high as 22 % of it's total removal in mega-cities where NO_x emissions are high.
  - NO_3 is an important nighttime oxidant. The yield formed from Criegee + NO_2 has been estimated to yield up to ~ 40 % of that produced via the principal pathway, O_3 + NO_2.

- **Assumes 100 % yield of NO_3 form the reaction - laboratory studies of the reaction products are inconsistent and conflicting.**

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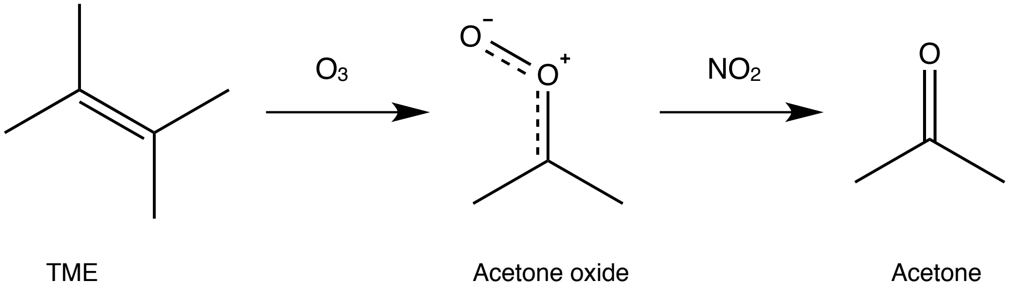
- Presto and Donahue observed **enhanced acetone yields** at higher pressure and TME consumption in the ozonolysis of TME in the presence of NO_2.



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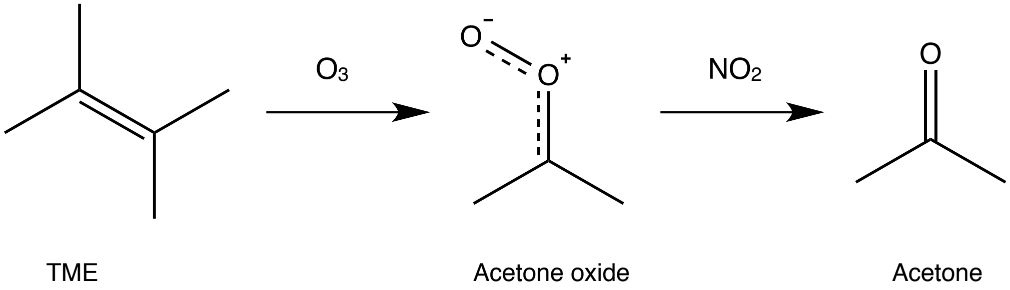

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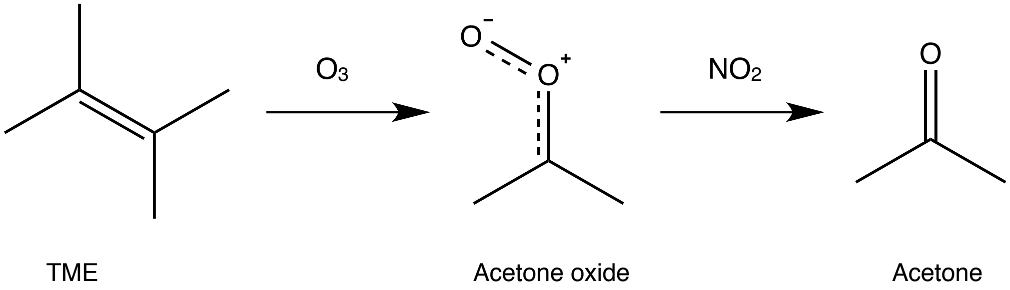

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  - Attributed to CH_2IOONO_2 which is thought to inhibit formaldehyde formation.

$$\left.\begin{array}{l} \mathrm{RCR'I} + O_2 \longrightarrow \mathrm{RCR'OO} + \mathrm{I} \\ \mathrm{RCR'I} + O_2 \longrightarrow \mathrm{RCR'IOO} \end{array}\right\} \textit{Pressure dependent}$$

$$\mathrm{RCR'IOO} + NO_2 \longrightarrow \mathrm{Products}$$

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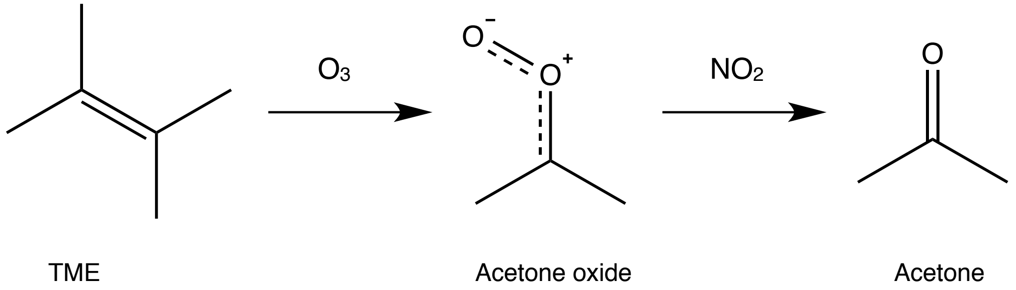

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- To date the only direct study which has provided evidence for NO_3 production is steady-state Broadband Cavity Enhanced Absorption Spectroscopy study of formaldehyde oxide + NO_2 by Ouyang *et al.*

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

  - Two detection cells were utilized: (a) NO_3 (ambient temperature) (b) NO_3 + N_2O_5 (358 K)

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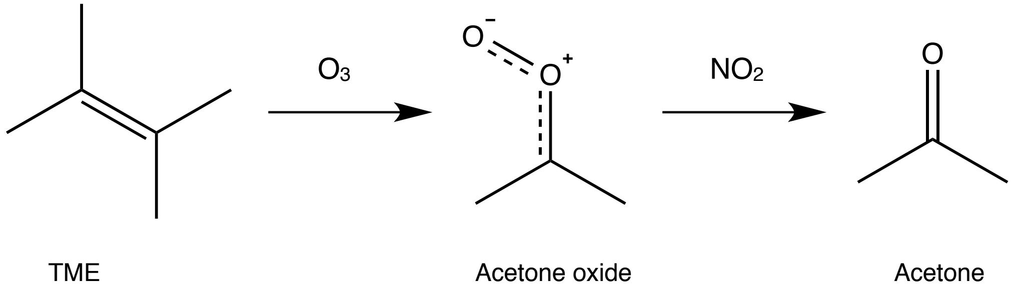

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- More recent time-resolved UV-Vis absorption study by Lewis *et al.* found little NO_3 generated in the formaldehyde oxide system, and that the observed **NO_3 could be rationalized by side chemistry.**

$$IONO_2 + INO_2 \longrightarrow NO_3 + NO_2 + I_2$$

- **To fully assess the impact of this reaction in the atmosphere, the products, as well as the kinetics, need to be understood.**

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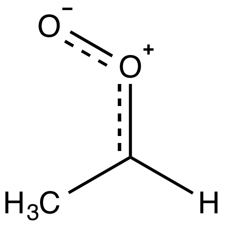
1. **MPIMS experimental studies**
   - Kinetic and product studies conducted for acetaldehyde oxide + NO_2 at 300 K (4, 20 and 40 Torr).
   - Product studies for formaldehyde oxide at 300 K, 4, 20 and 40 Torr.
   - Photolytic production of Criegee Intermediates from diiodoalkane photolysis at 248 nm (NO_2 cross section minimum) in the presence of O_2
   - Pseudo first order conditions maintained such that **$[NO_2] >> [\text{Criegee}]$ and $[O_2] >> [NO_2]$ to promote RCR'I + O_2 above RCR'I + NO_2**.
   - **Rate coefficients obtained via direct monitoring of Criegee Intermediate decay measured using 10.5 eV photoionization** (primarily *syn* conformer of acetaldehyde oxide).
   - NO_3 detection attempted via 13.0 eV photoionization measurements.
   - **Product characterization via 3D datasets (photon energy, m/z, kinetic time)** obtained by scanning the tunable VUV-photoionization output of the Advanced Light Source in 25 meV increments. Allows **isomeric resolution** using calculated and measured reference photoionization energy spectra, which are unique to each molecule.
   - Orthogonal-acceleration time of flight detection



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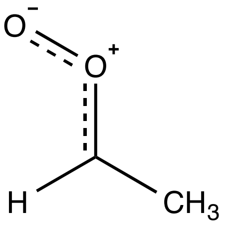

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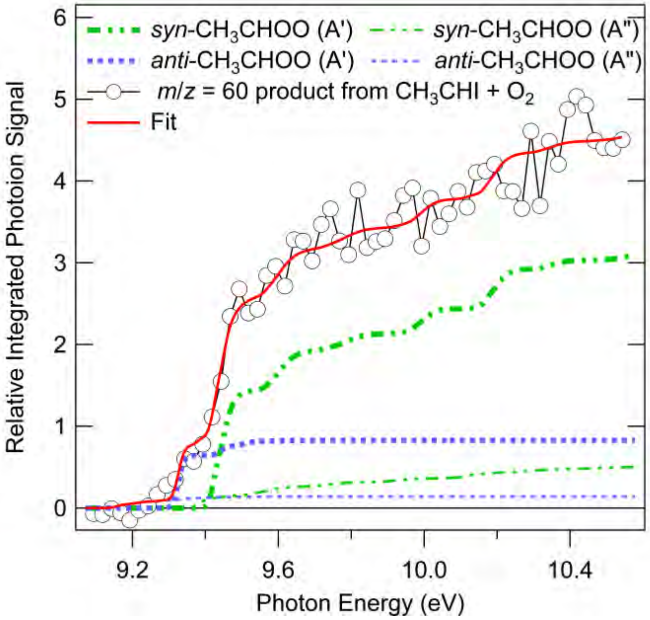

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2. ***Ab initio* calculations (Papajak)**
    - Stationary point calculations and adiabatic ionization energy calculations performed at the ωB97XD/6-31+G(d) level of density functional theory or using ωB97XD/ADZP to help to identify product chemical structures and the sources of observed experimental signals.

J.-D. Chai and M. Head-Gordon, *The Journal of Chemical Physics*, 2008, 128, 084106.
J.-D. Chai and M. Head-Gordon, *Physical Chemistry Chemical Physics*, 2008, 10, 6615-6620.
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Approach

1. **MPIMS experimental studies**
    - Kinetic and product studies conducted for acetaldehyde oxide + NO_2 at 300 K (4, 20 and 40 Torr).
    - Product studies for formaldehyde oxide at 300 K, 4, 20 and 40 Torr.
    - Photolytic production of Criegee Intermediates from diiodoalkane photolysis at 248 nm (NO_2 cross section minimum) in the presence of O_2
    - Pseudo first order conditions maintained such that [**NO_2]>>[Criegee] and [O_2]>>[NO_2] to promote RCR'I + O_2 above RCR'I + NO_2**.
    - **Rate coefficients obtained via direct monitoring of Criegee Intermediate decay measured using 10.5 eV photoionization** (primarily *syn* conformer of acetaldehyde oxide).
    - NO_3 detection attempted via 13.0 eV photoionization measurements.
    - **Product characterization via 3D datasets (photon energy, m/z, kinetic time)** obtained by scanning the tunable VUV-photoionization output of the Advanced Light Source in 25 meV increments. Allows **isomeric resolution** using calculated and measured reference photoionization energy spectra, which are unique to each molecule.
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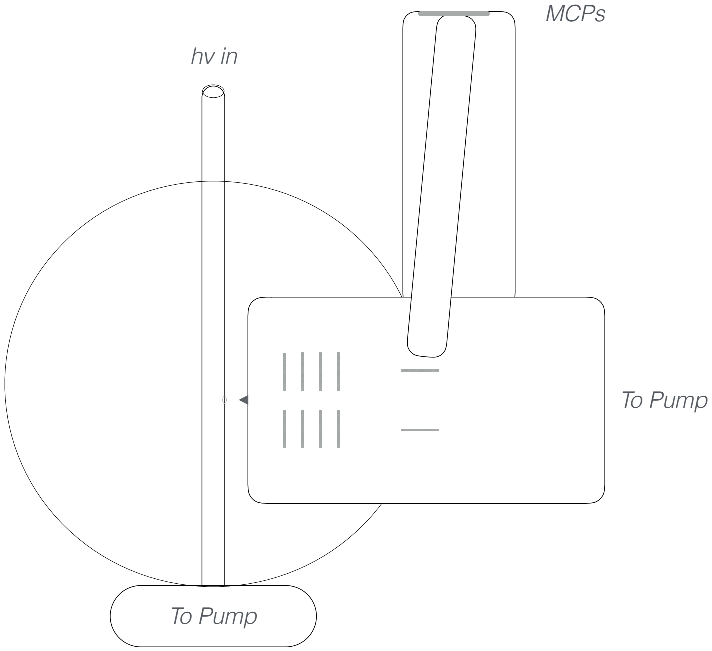
2. ***Ab initio* calculations (Papajak)**
    - Stationary point calculations and adiabatic ionization energy calculations performed at the ωB97XD/6-31+G(d) level of density functional theory or using ωB97XD/ADZP to help to identify product chemical structures and the sources of observed experimental signals.

3. **Global modeling work (Khan & Shallcross)**
    - STOCHEM-CRI : 3D chemical transport model to assess the potential impact of Criegee intermediate + NO_2 reactions.
    - Criegee intermediate concentrations calculated using SSA
        - Total production rate is equivalent to $k_{O3+alkene}[alkene_x][O_3]\alpha$, where α is yield of stabilized Criegee Intermediate
        - Total loss rate is $(k_{uni} + k_{Criegee+H2O}[H_2O])$
        - Fast reaction of formaldehyde oxide with water dimer accounted for in the model

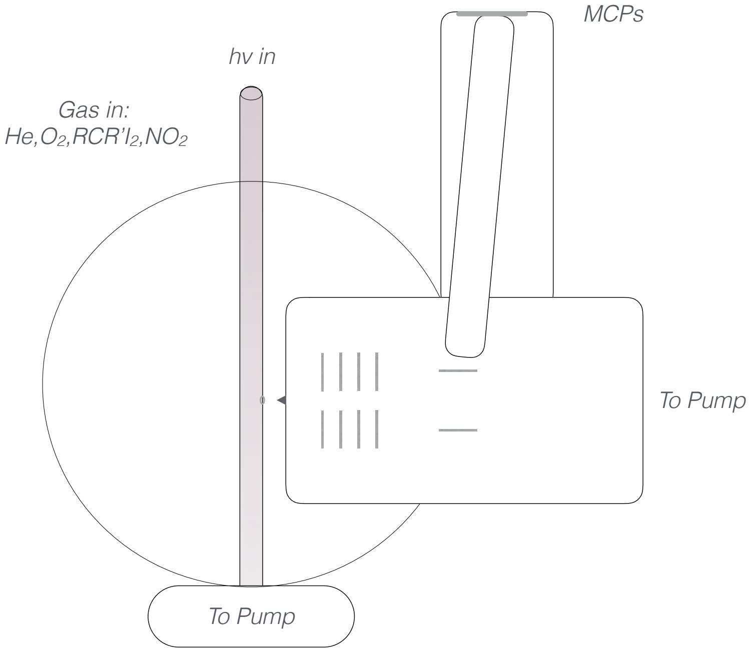
C. Granier, J. Lamarque, A. Mieville, J. Muller, J. Olivier, J. Orlando, J. Peters, G. Petron, G. Tyndall and S. Wallens, POET, a database of surface emissions of ozone precursors, 2005., S. R. Utembe, M. C. Cooke, A. T. Archibald, M. E. Jenkin, R. G. Derwent and D. E. Shallcross, *Atmospheric Environment*, 2010, 44, 1609-1622., S. R. Utembe, M. C. Cooke, A. T. Archibald, D. E. Shallcross, R. G. Derwent and M. E. Jenkin, *Atmospheric environment*, 2011, 45, 1604-1614., S. R. Utembe, L. A. Watson, D. E. Shallcross and M. E. Jenkin, *Atmospheric Environment*, 2009, 43, 1982-1990., L. A. Watson, D. E. Shallcross, S. R. Utembe and M. E. Jenkin, *Atmospheric Environment*, 2008, 42, 7196-7204., M. E. Jenkin, L. A. Watson, S. R. Utembe and D. E. Shallcross, *Atmospheric Environment*, 2008, 42, 7185-7195., R. Derwent, D. Stevenson, R. Doherty, W. Collins and M. Sanderson, *Atmospheric Environment*, 2008, 42, 7412-7422., W. Collins, D. S. Stevenson, C. Johnson and R. Derwent, *Journal of Atmospheric Chemistry*, 1997, 26, 223-274., T. C. Johns, R. E. Carnell, J. F. Crossley, J. M. Gregory, J. F. Mitchell, C. A. Senior, S. F. Tett and R. A. Wood, *Climate dynamics*, 1997, 13, 103-134., W. Chao, J.-T. Hsieh, C.-H. Chang and J.-J. M. Lin, *Science*, 2015, 347, 751-754.

Sandia Multiplexed Photoionization Mass Spectrometer



Halocarbon wax coated quartz reactor permits operating conditions of **~1-40 Torr, 300-373 K.**

Sandia Multiplexed Photoionization Mass Spectrometer



Halocarbon wax coated quartz reactor permits operating conditions of **~1-40 Torr, 300-373 K.**

Reactants, intermediates and products fare continuously sampled via small pinhole in side wall of quartz reactor.

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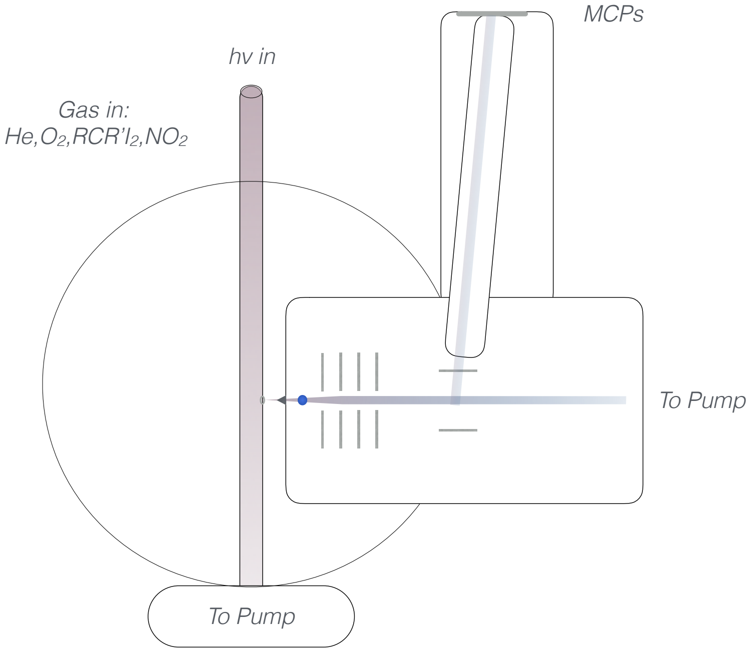


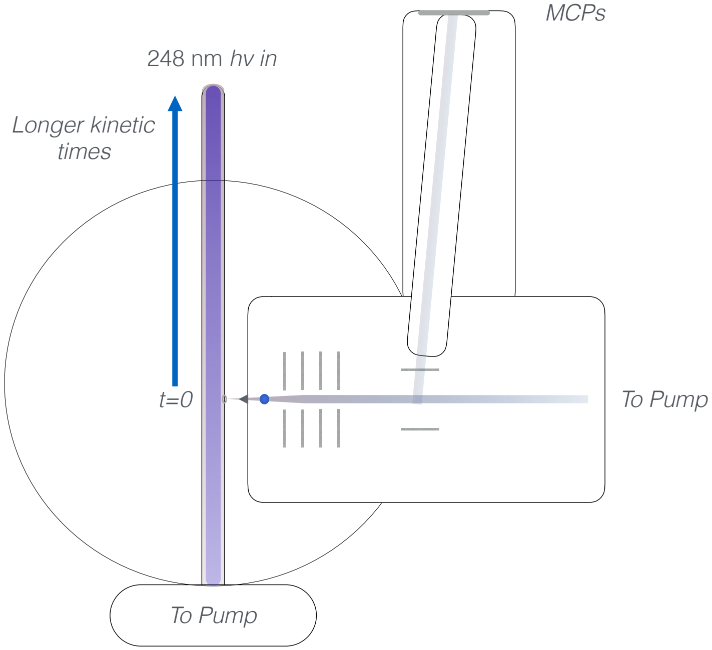
Halocarbon wax coated quartz reactor permits operating conditions of **~1-40 Torr, 300-373 K.**

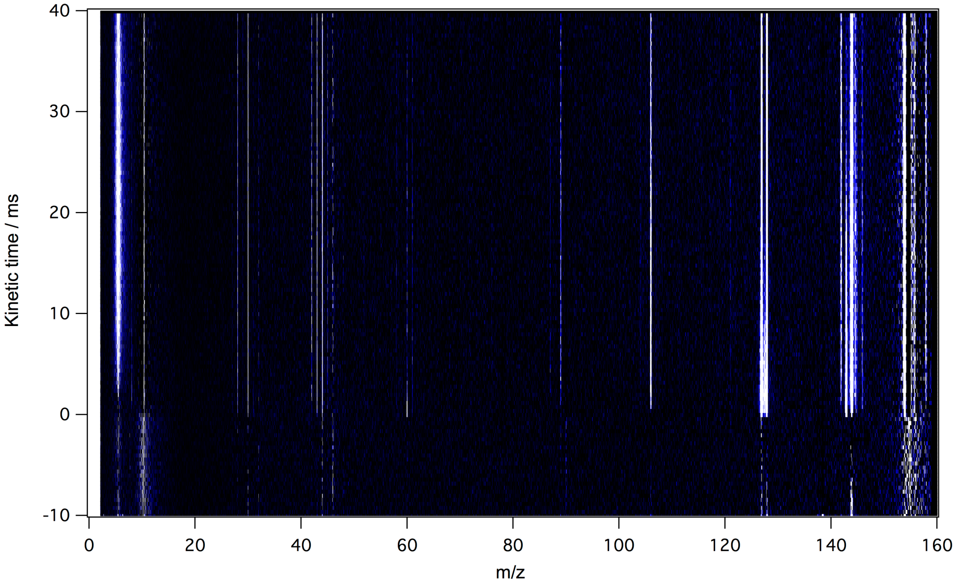
Reactants, intermediates and products fare continuously sampled via small pinhole in side wall of quartz reactor.

Gas enters ionization region via skimmer where it is intercepted by **pseudo-continuous tunable VUV radiation (~7-15 eV typical)**.

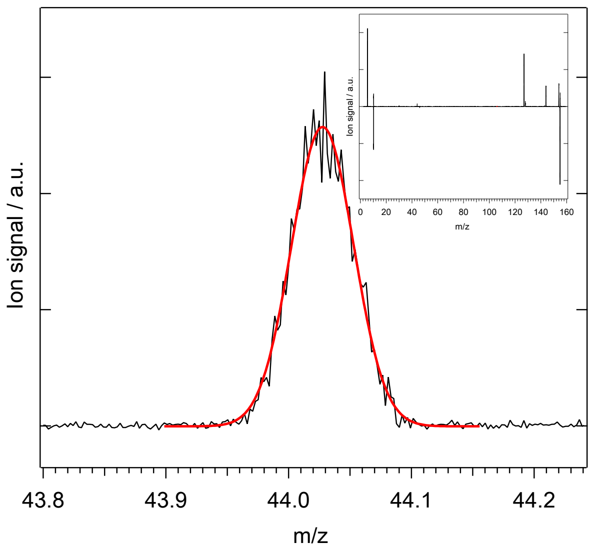
Ions are subsequently detected via orthogonal-acceleration TOF mass spectrometry.

3D datasets from MPIMS

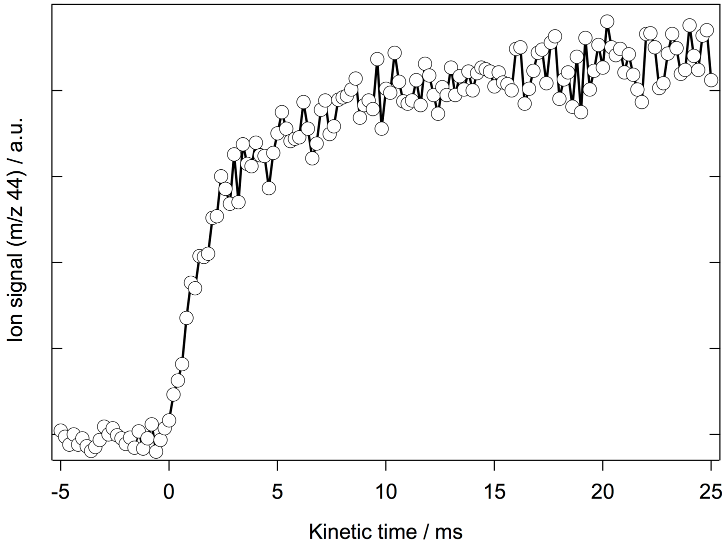




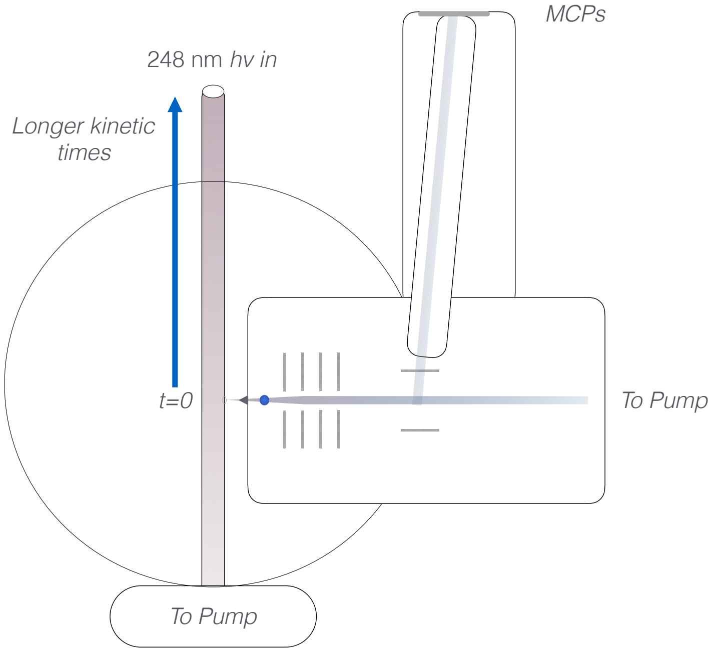
High resolution mass spectra

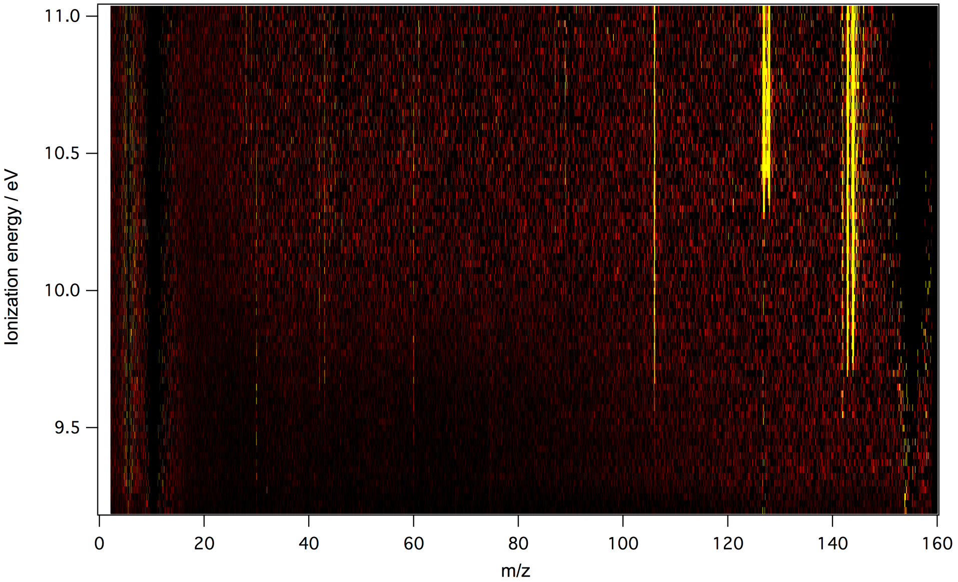


Kinetic profiles

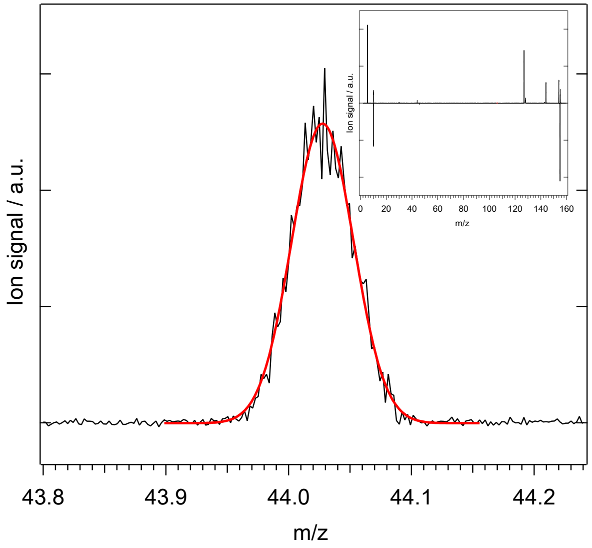


3D datasets from MPIMS

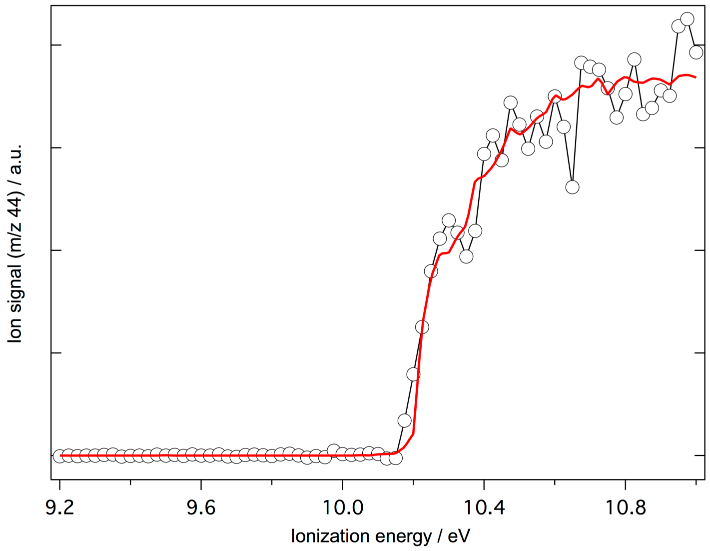




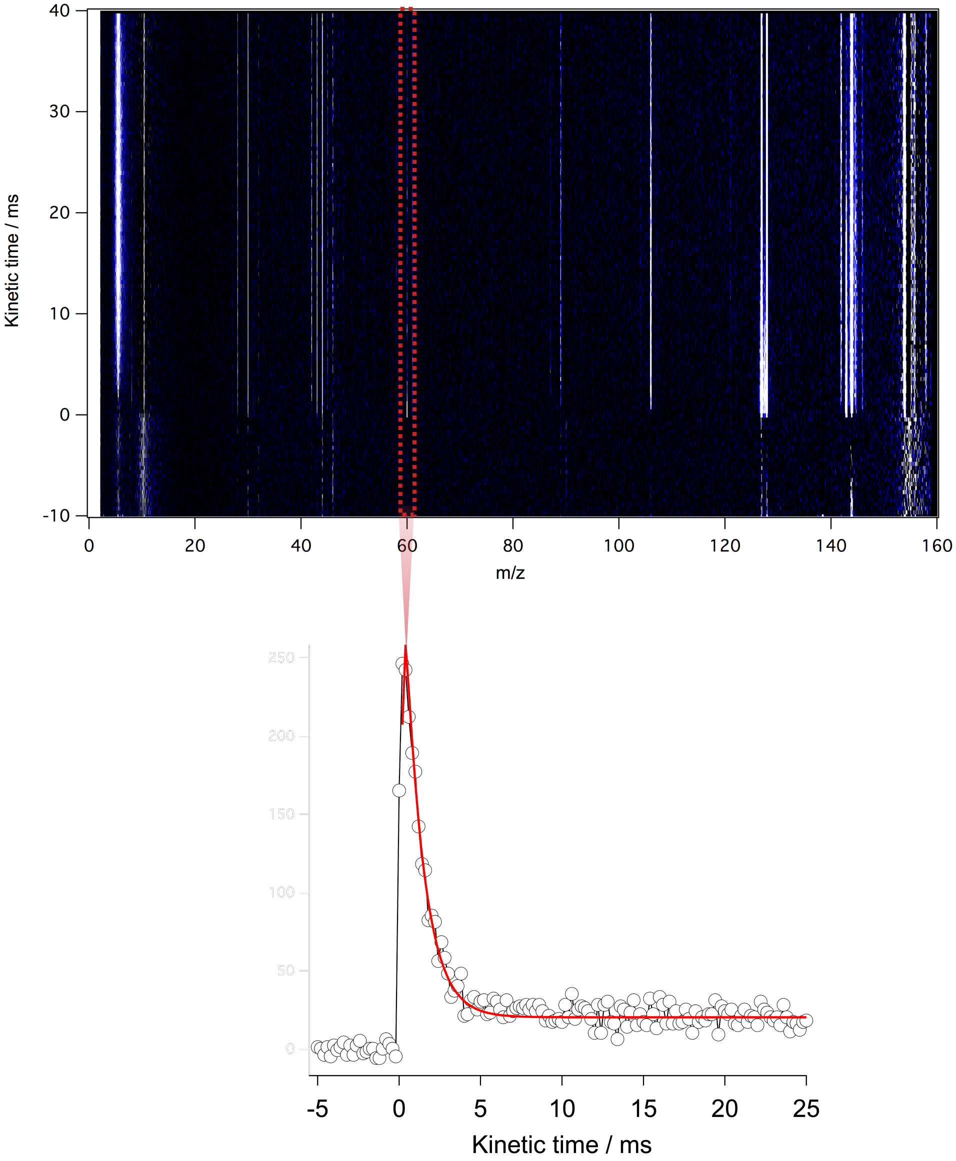
High resolution mass spectra



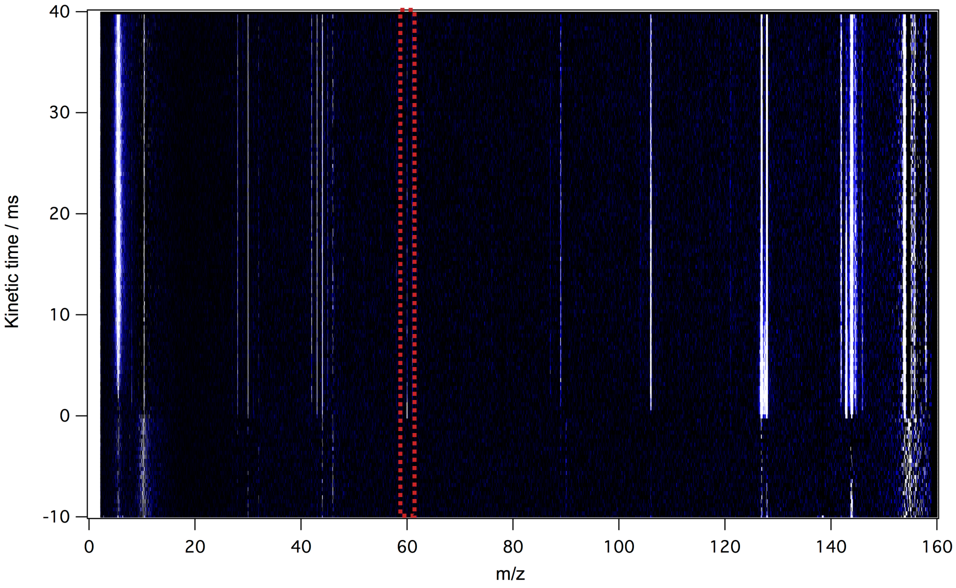
PI spectra for isomer assignment

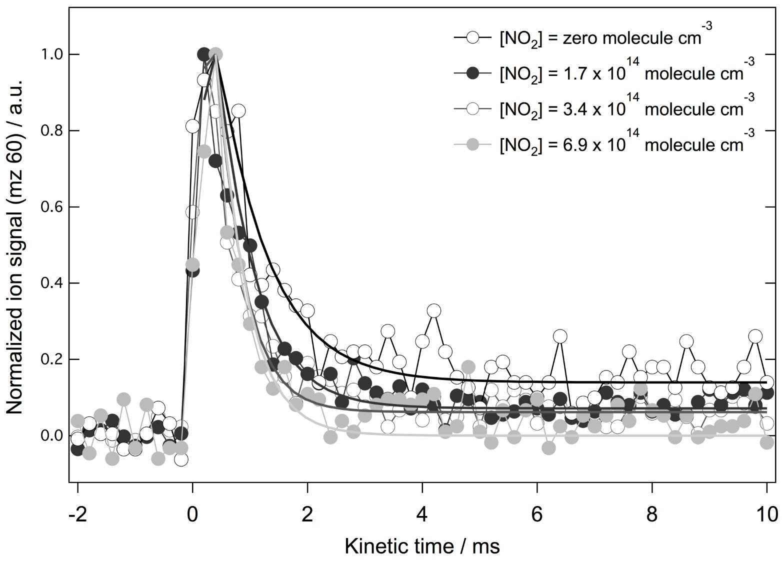


Kinetics of Acetaldehyde Oxide + NO_2



Kinetics of Acetaldehyde Oxide + NO_2





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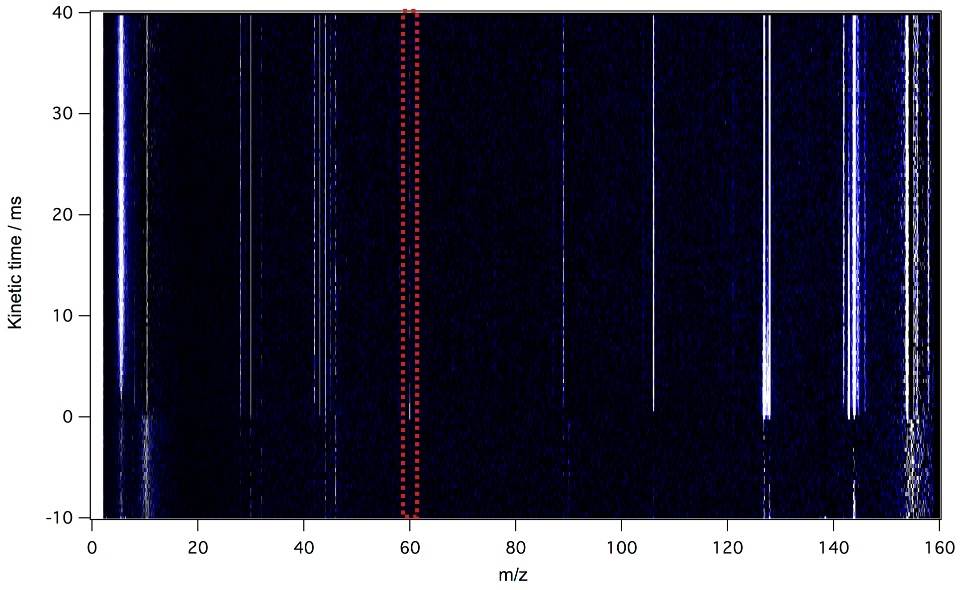

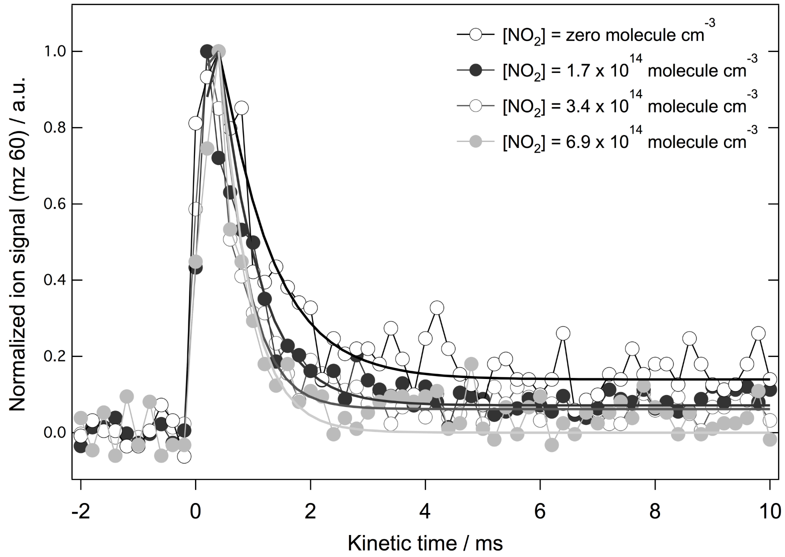

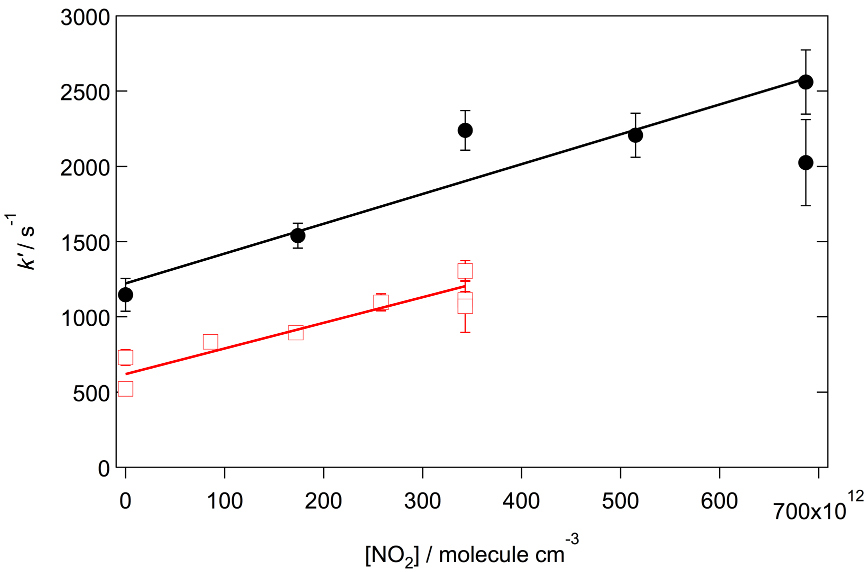

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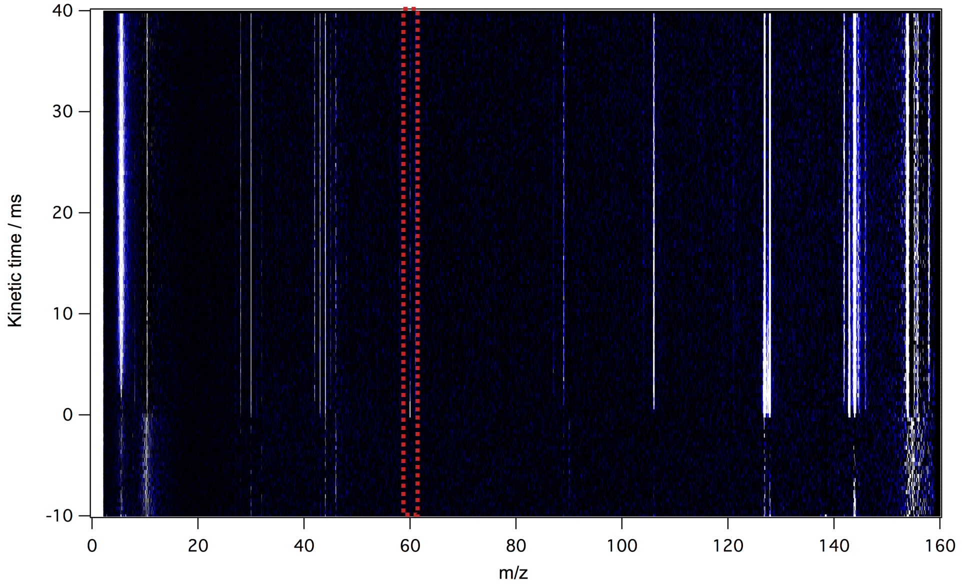
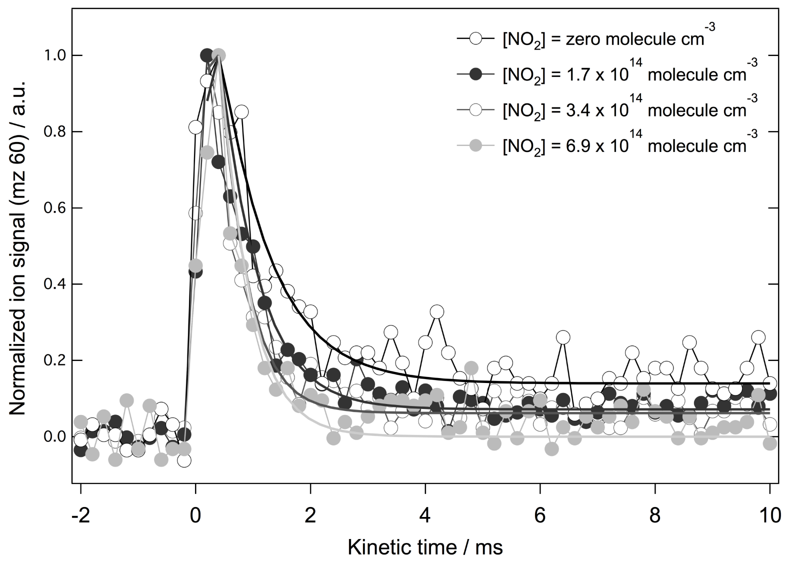
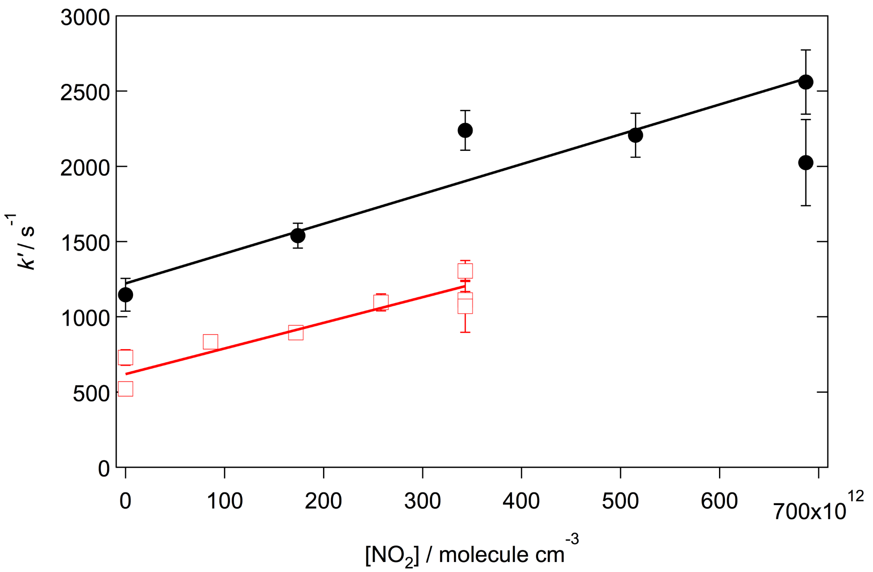


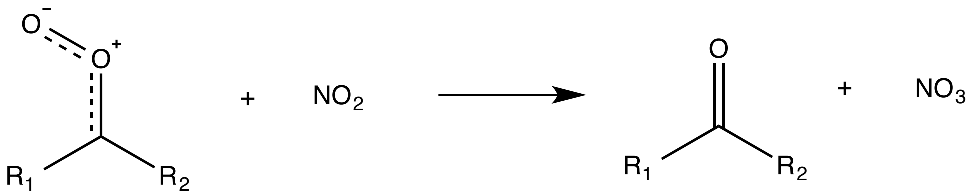




Criegee		**P /Torr**	***k*** **/ 10^{-12} molecule^{-1} cm^3 s^{-1}**
Formaldehyde oxide	Welz *et al.*	4	7 (+3, -2)
	Stone *et al.*	25-300	1.5 ± 0.5
Acetaldehyde oxide	Taatjes *et al.*	4	2 ± 1
	This work	20	1.7 ± 0.3
		40	2.0 ± 0.7
Acetone oxide	Chhantyal-Pun *et al.*	4	≤ 5

O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross and C. A. Taatjes, *Science*, 2012, 335, 204-207.
D. Stone, M. Blitz, L. Daubney, N. U. Howes and P. Seakins, *Physical Chemistry Chemical Physics*, 2014, 16, 1139-1149.
C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.
R. Chhantyal-Pun, O. Welz, J. D. Savee, A. J. Eskola, E. P. Lee, L. Blacker, H. R. Hill, M. Ashcroft, M. A. H. Khan, G. C. Lloyd-Jones, L. Evans, B. Rotavera, H. Huang, D. L. Osborn, D. K. W. Mok, J. M. Dyke, D. E. Shallcross, C. J. Percival, A. J. Orr-Ewing and C. A. Taatjes, *The Journal of Physical Chemistry A*, 2016.
R. L. Caravan, M. A. H. H. Khan, B. Rotavera, E. Papajak, I. Antonov, M.-W. Chen, K. Au, W. Chao, D. L. Osborn, J.-J. M. Lin, C. J. Percival, D. E. Shallcross and C. A. Taatjes, *Faraday discussions*, 2017, Accepted.

Products of Acetaldehyde Oxide + NO_2 : Acetaldehyde + NO_3



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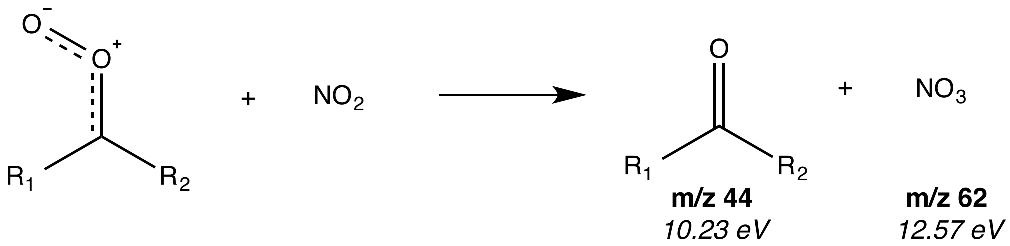

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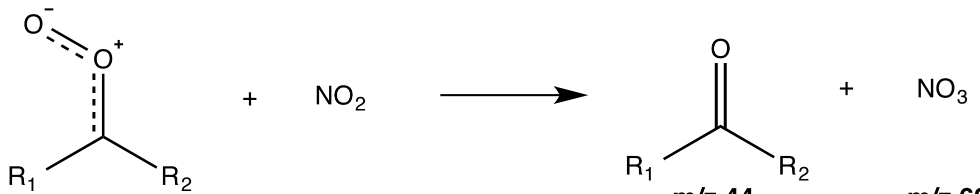

m/z 44
10.23 eV

m/z 62
12.57 eV

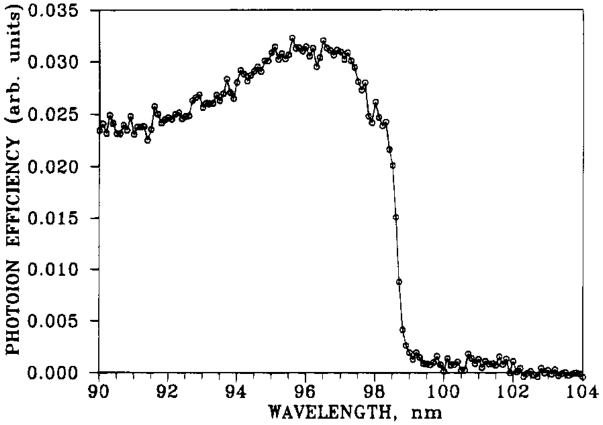

Figure 3. Photoionization efficiency spectrum of NO_3 between λ = 90.0 and 104.0 nm obtained at a nominal resolution of 0.23 nm and with 0.1 nm steps. The photoion efficiency is the ion counts at m/z = 62 divided by the light intensity in arbitrary units.

Reproduced from Monks et al., JPC, 1994.

P. Monks, L. Stief, M. Krauss, S. Kuo, Z. Zhang and R. Klemm, *The Journal of Physical Chemistry*, 1994, 98, 10017-10022.

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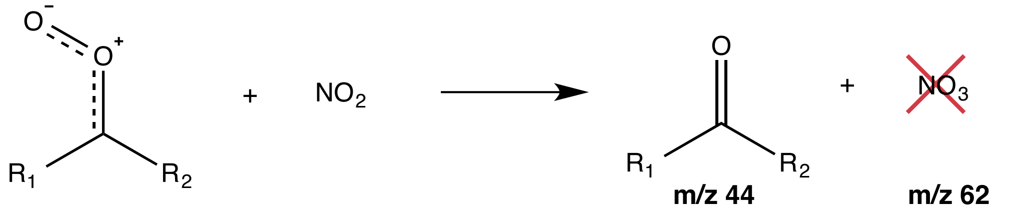
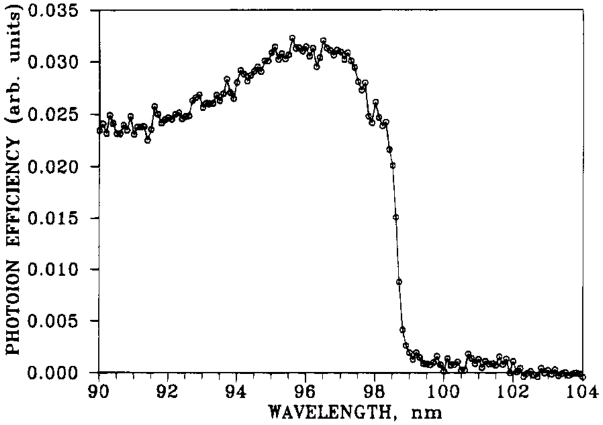


m/z 44
10.23 eV

m/z 62
12.57 eV



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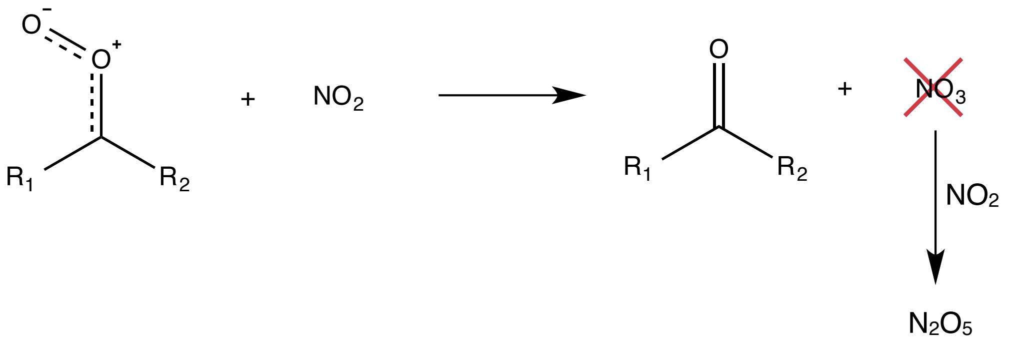


m/z 108

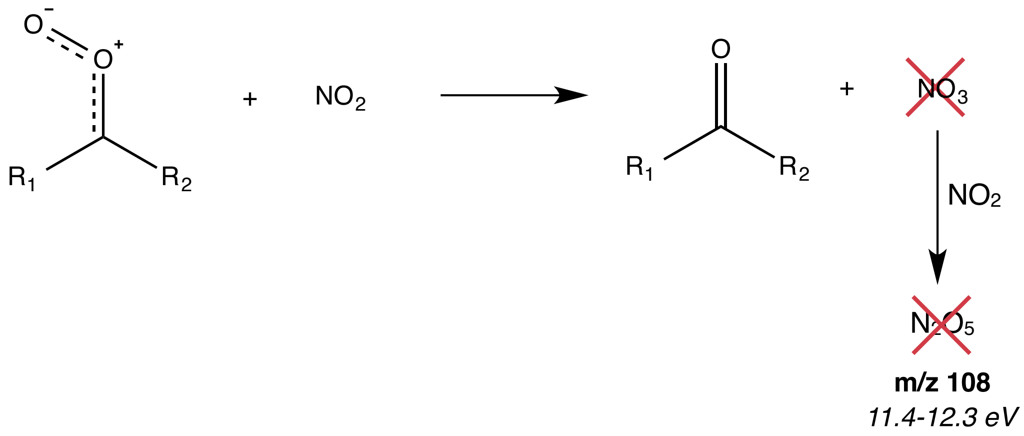
11.4-12.3 eV

Reaction with NO_2 ~ 16 % of NO_3 loss under our experimental conditions

(~ 2×10^{-12} molecule^{-1} cm^{3} s^{-1} at 40 Torr He)

B. Ouyang, M. W. McLeod, R. L. Jones and W. J. Bloss, *Physical Chemistry Chemical Physics*, 2013, 15, 17070-17075.
D. Ames and D. Turner, *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 1976, 348, 175-186.
S. G. Lias, J. E. Bartmess, J. F. Liebman and J. L. Holmes, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, eds. R. Levin and W. Mallard, National Institute of Standards and Technology,Gaithersburg MD, 2003, vol. 20899.

Products of Acetaldehyde Oxide + NO_2 : Acetaldehyde + NO_3



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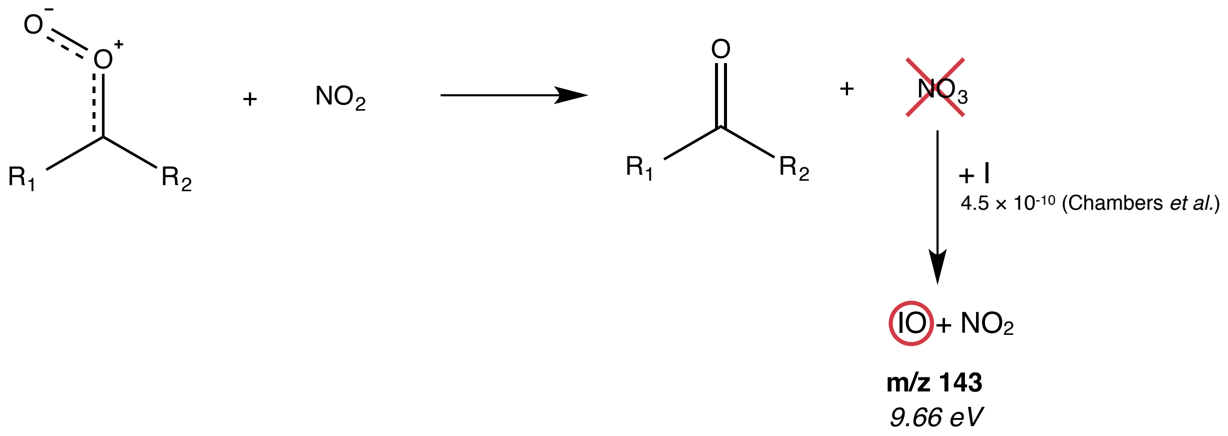
Products of Acetaldehyde Oxide + NO_2 : Acetaldehyde + NO_3



+ I
4.5 × 10^{-10} (Chambers *et al.*)

IO + NO_2

m/z 143
9.66 eV

Reaction with NO_2 ~ 16 % of NO_3 loss under our experimental conditions
(~ 2 × 10^{-12} molecule^{-1} cm^3 s^{-1} at 40 Torr He)

Dominant loss would be mostly due to reaction with I

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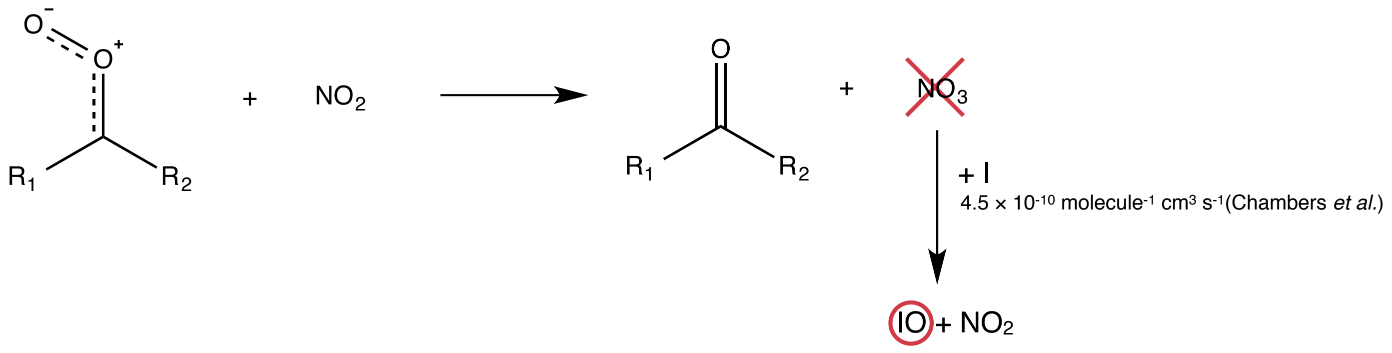
D. Ames and D. Turner, *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 1976, 348, 175-186.
S. G. Lias, J. E. Bartmess, J. F. Liebman and J. L. Holmes, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, eds. R. Levin and W. Mallard, National Institute of Standards and Technology,Gaithersburg MD, 2003, vol. 20899.
R. Chambers, A. Heard and R. Wayne, *The Journal of Physical Chemistry*, 1992, 96, 3321-3331.

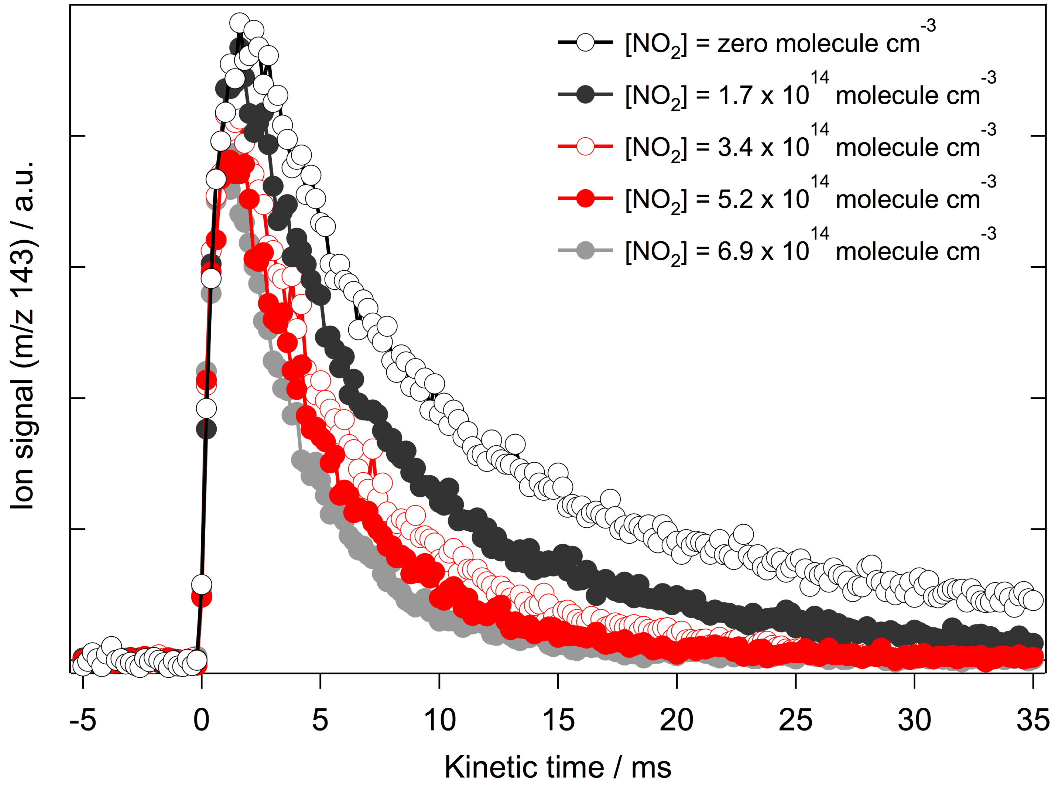
Products of Acetaldehyde Oxide + NO_2 : Acetaldehyde + NO_3



4.5×10^{-10} molecule^{-1} cm^3 s^{-1}(Chambers *et al.*)

m/z 143

9.66 eV



Reaction with NO_2 ~ 16 % of NO_3 loss under our experimental conditions
(~ 2×10^{-12} molecule^{-1} cm^3 s^{-1} at 40 Torr He)

Dominant loss would be mostly due to reaction with I

IO signal amplitude **decreases** and k_{loss} **increases** with $[NO_2]$

IO could be produced and lost via a number of reaction pathways, *i.e*;

$$CH_3CHOO + I \longrightarrow CH_3CHO + IO$$

$$CH_3CHIOO + I \longrightarrow CH_3CHO + IO + I$$

Inconclusive

B. Ouyang, M. W. McLeod, R. L. Jones and W. J. Bloss, *Physical Chemistry Chemical Physics*, 2013, 15, 17070-17075.
D. Ames and D. Turner, *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 1976, 348, 175-186.
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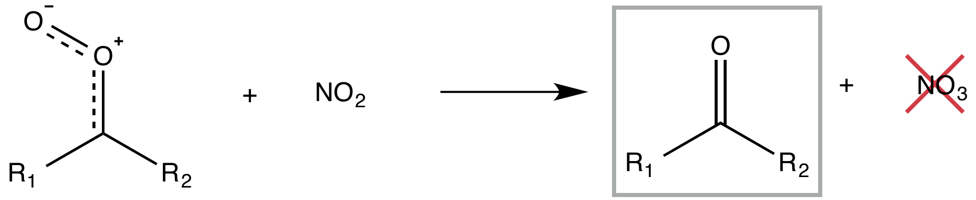
Products of Acetaldehyde Oxide + NO$_2$: Acetaldehyde + NO$_3$

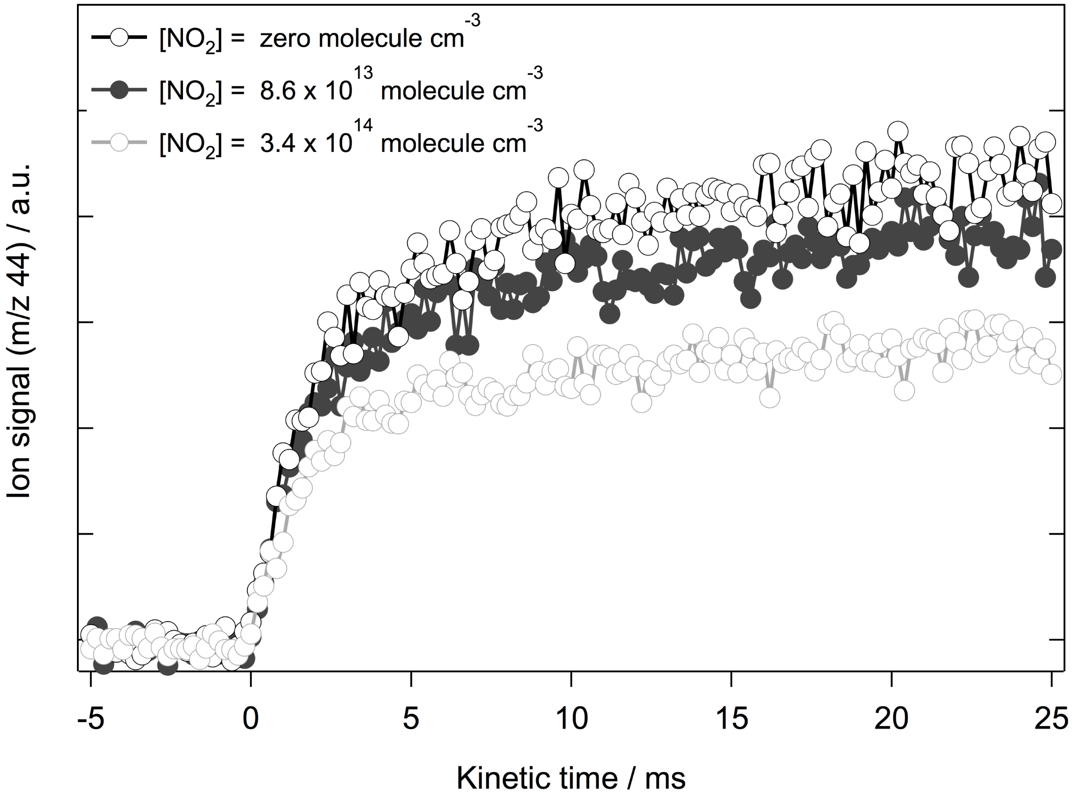


$$CH_3CHIOO + I \longrightarrow CH_3CHO + IO + I$$

$$CH_3CHIOO + CH_3CHIOO \longrightarrow 2CH_3CHIO + O_2$$

$$CH_3CHIO \longrightarrow CH_3CHO + I$$

$$CH_3CHOO + I \longrightarrow CH_3CHO + IO$$



We observe a **reduction** in acetaldehyde signal as a *f*[NO2]

In line with the observations made by Stone *et al.*, Chhantyal-Pun *et al.*, and Taatjes *et al.*

We can utilize the change in acetaldehyde signal with [NO$_2$] as an estimate for an upper limit on the NO$_3$ yield.

D. Stone, M. Blitz, L. Daubney, N. U. Howes and P. Seakins, *Physical Chemistry Chemical Physics*, 2014, 16, 1139-1149.
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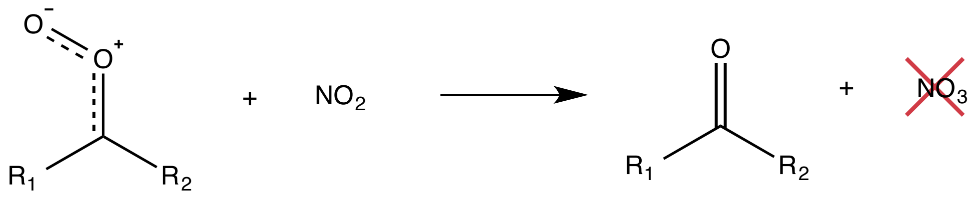
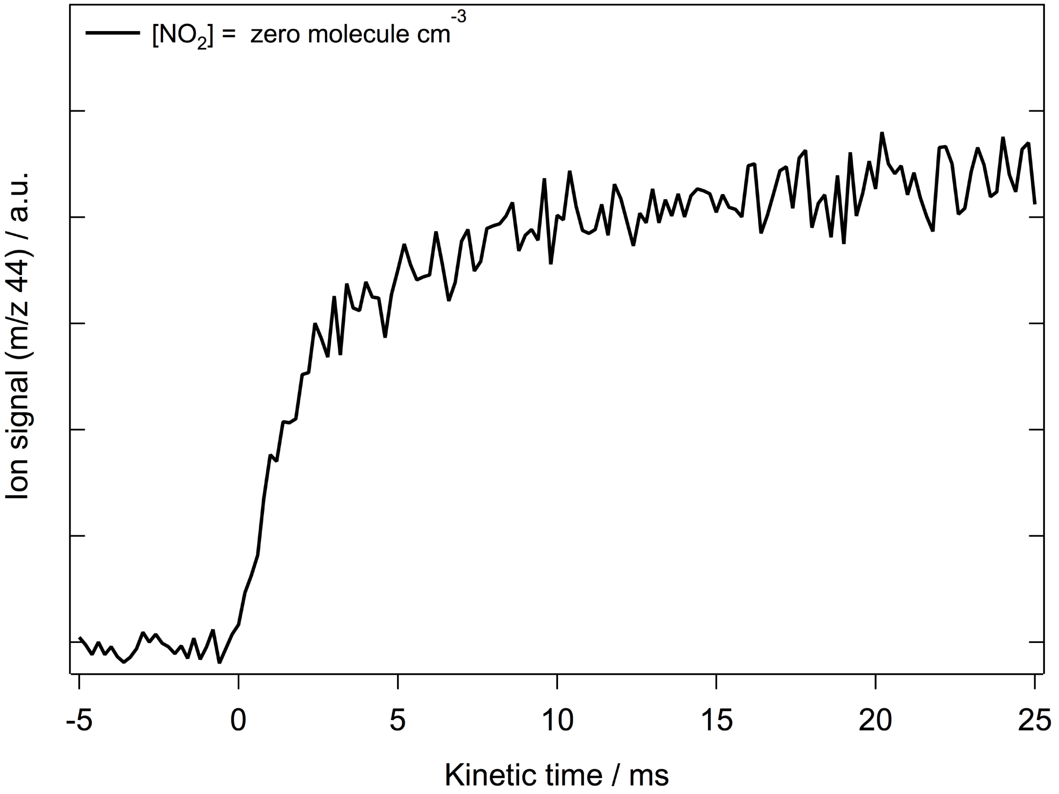
R. L. Caravan, M. A. H. H. Khan, B. Rotavera, E. Papajak, I. Antonov, M.-W. Chen, K. Au, W. Chao, D. L. Osborn, J.-J. M. Lin, C. J. Percival, D. E. Shallcross and C. A. Taatjes, *Faraday discussions*, 2017, Accepted.

Products of Acetaldehyde Oxide + NO_2 : Acetaldehyde + NO_3



$CH_3CHOO + I \longrightarrow \boxed{CH_3CHO} + IO$



From measured bimolecular rate coefficient, we can calculate the % loss of Criegee due to reaction with NO_2 at a given $[NO_2]$.

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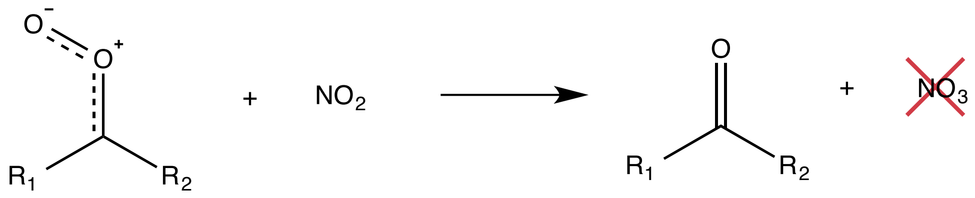

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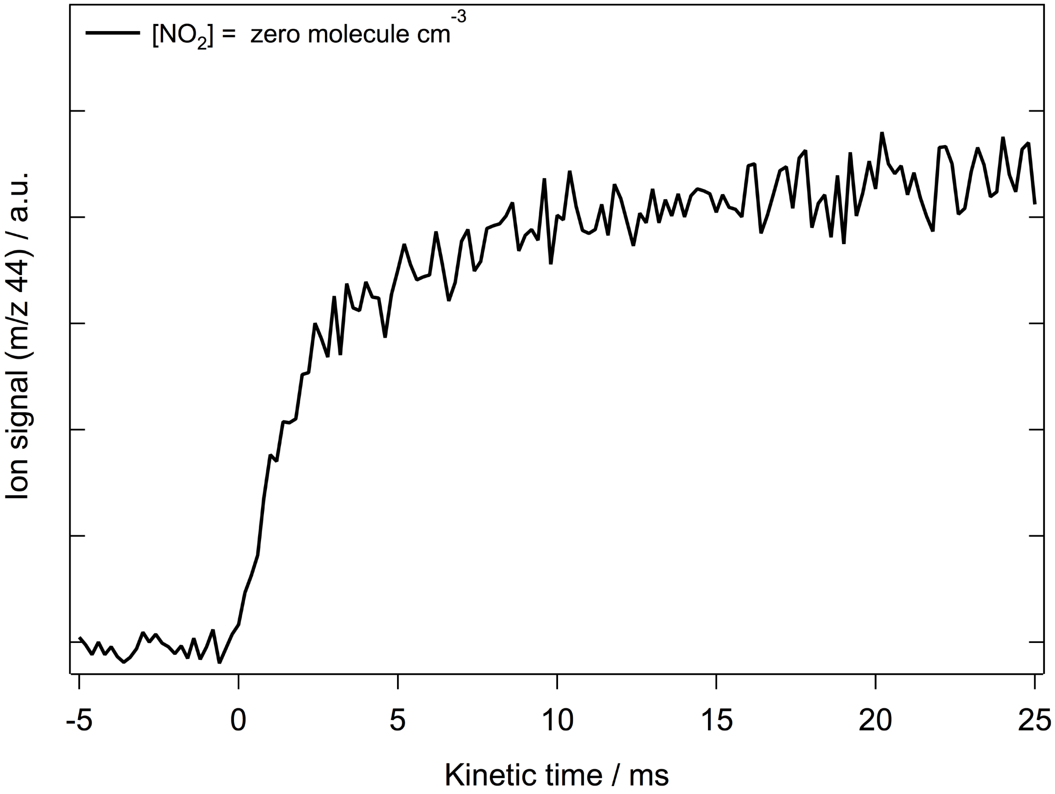

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% CI Loss due to reaction= $(k'_{NO2}/(k'_{NO2}+k'_{intercept})) \times 100$.

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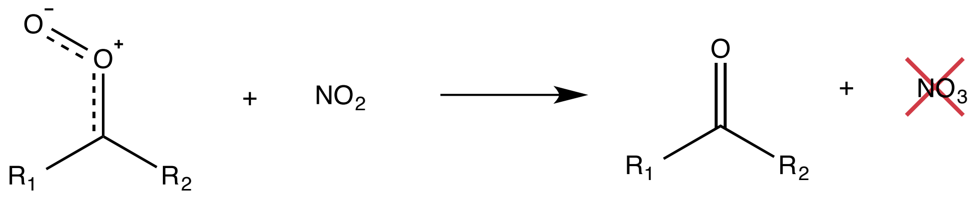

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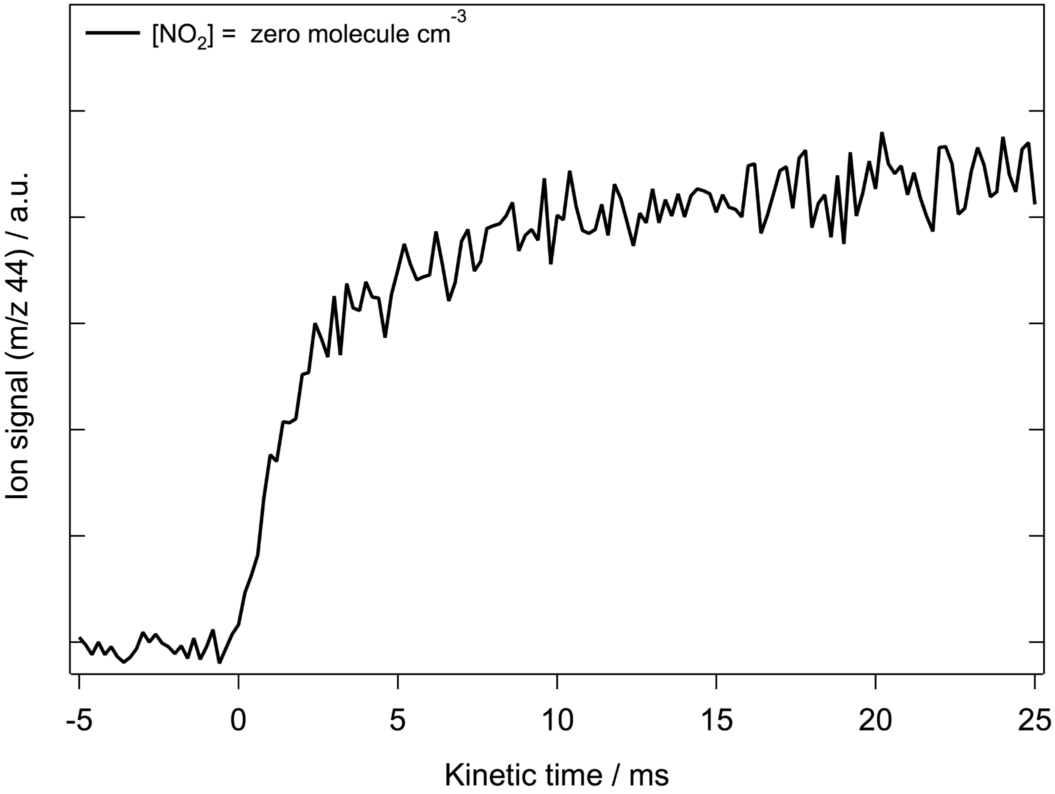

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The anticipated signal can be calculated by the following:

$Signal_{(NO2)}=Signal_{(no\ NO2)}$ x (100% - (% CI loss due to reaction x (1-yield)))

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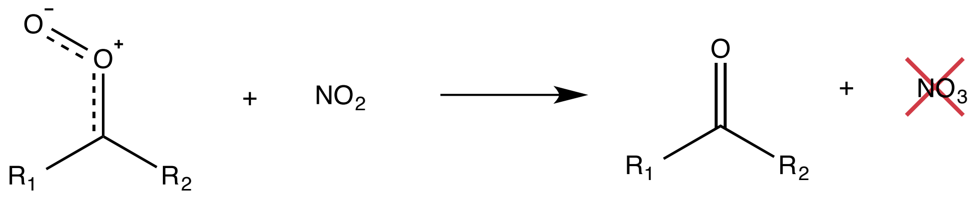

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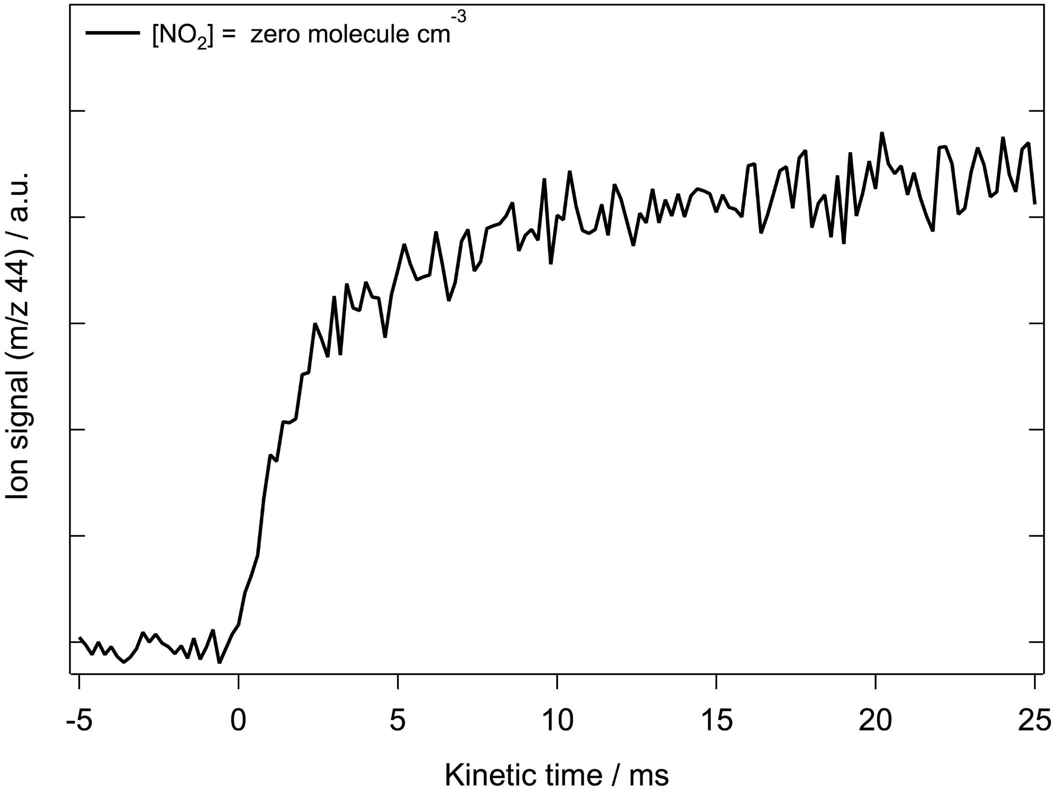

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The yield can be varied to simulate acetaldehyde signal profiles to compare with the measured experimental data.

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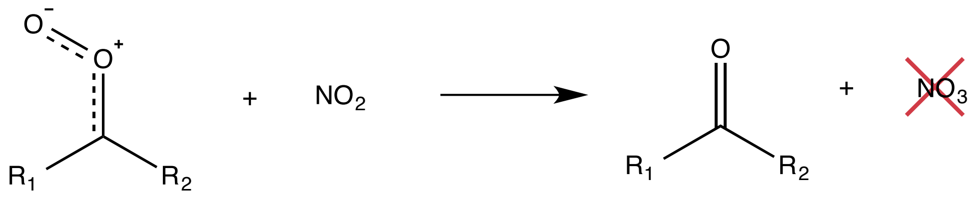

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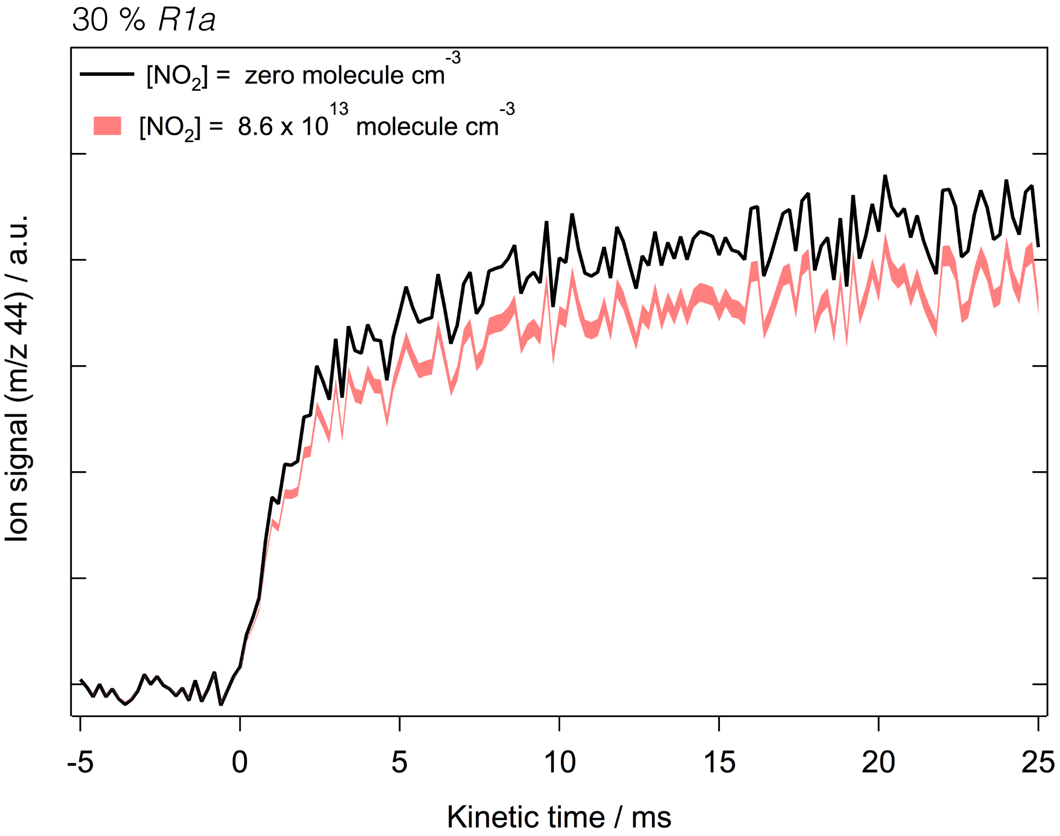

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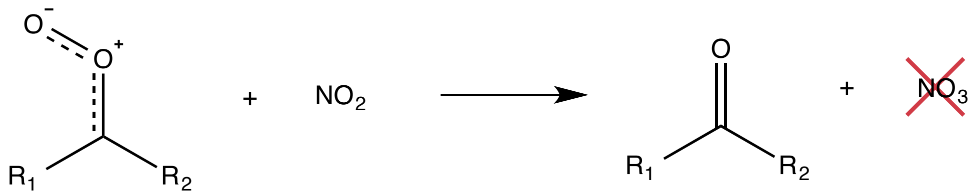
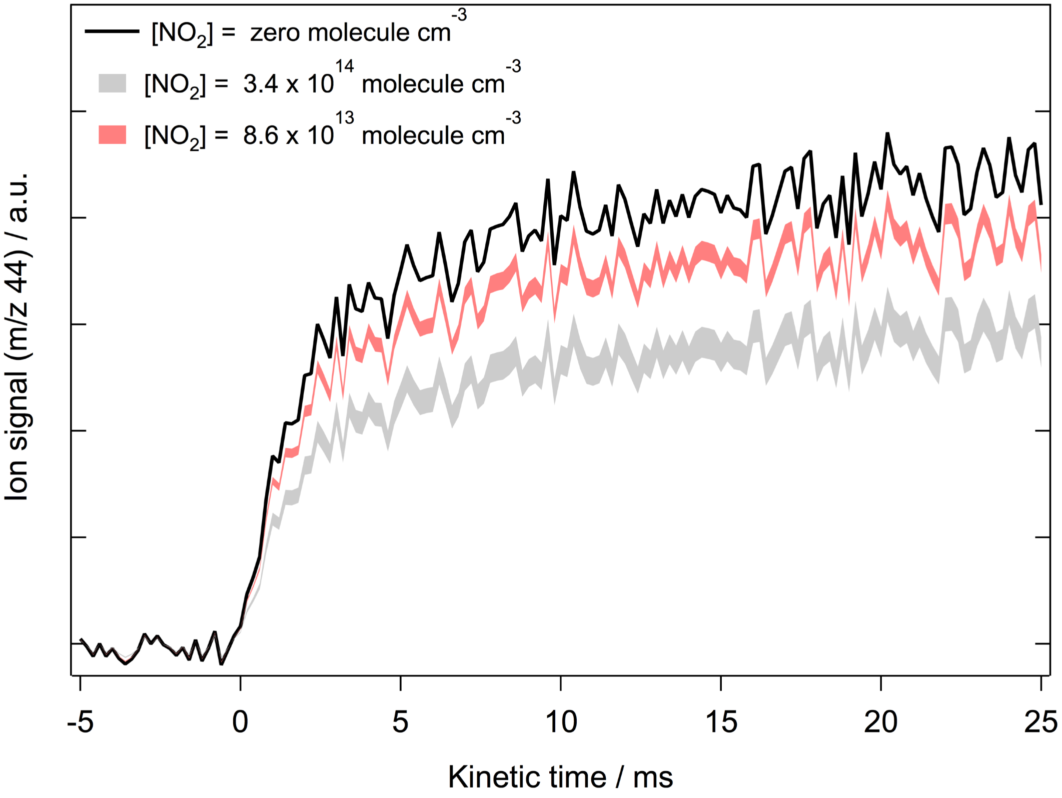


$$CH_3CHOO + I \longrightarrow \boxed{CH_3CHO} + IO$$

30 % *R1a*



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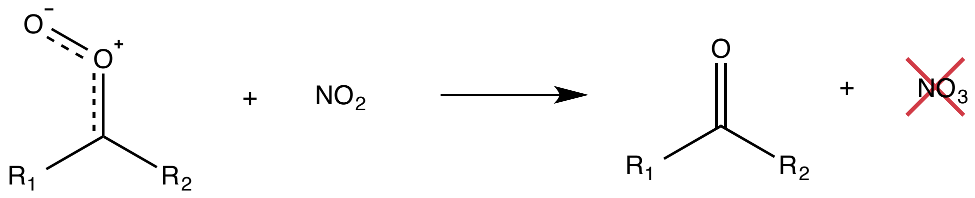

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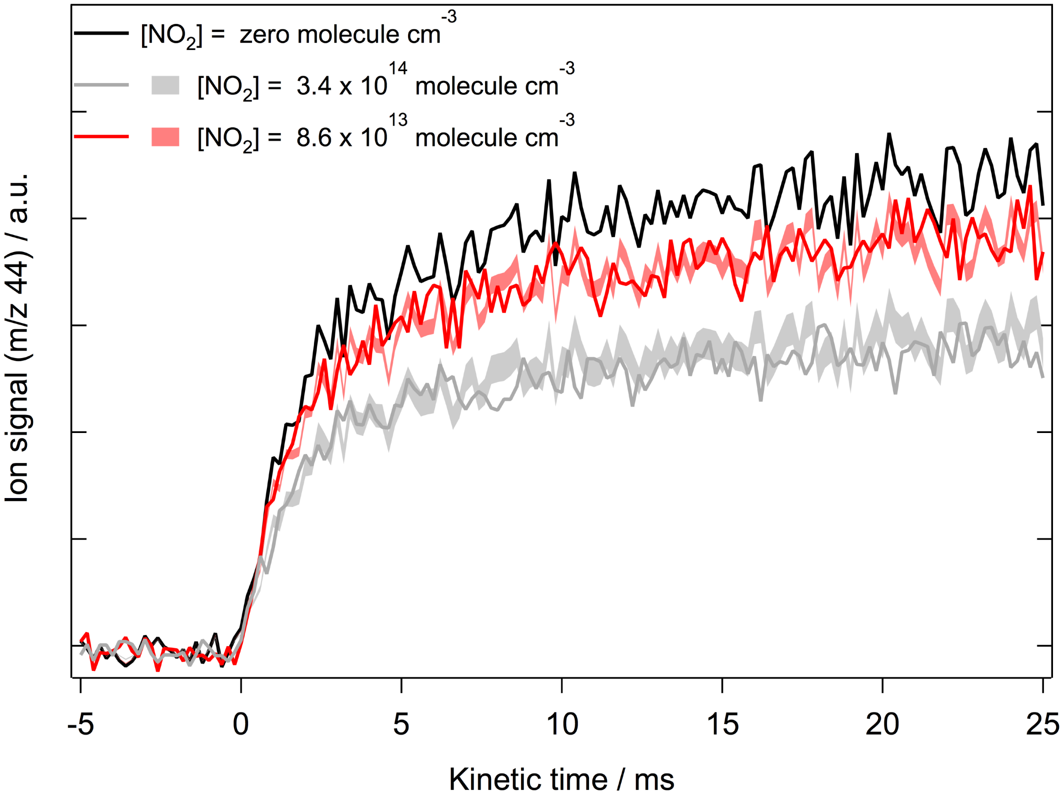

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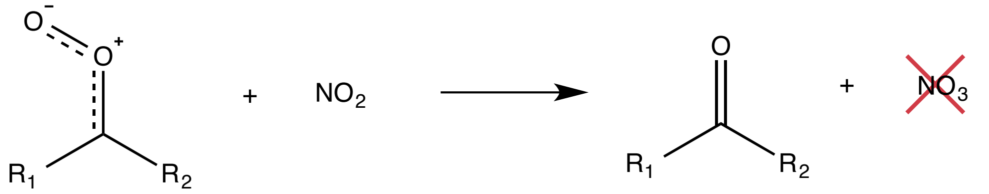
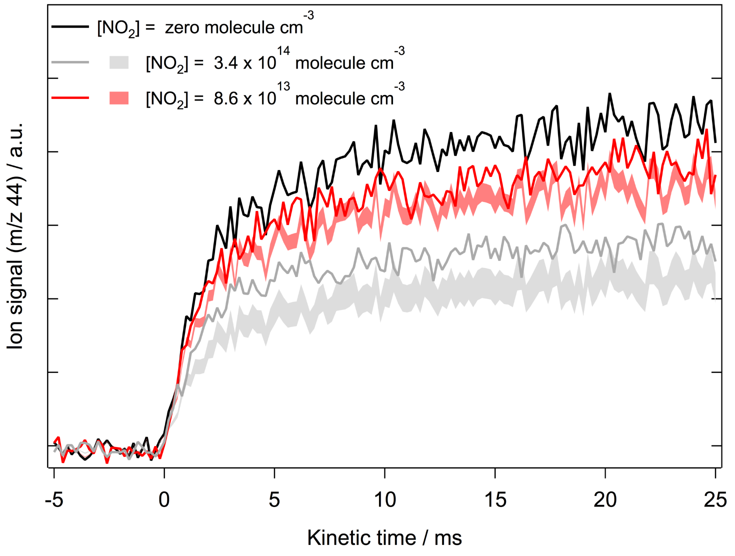
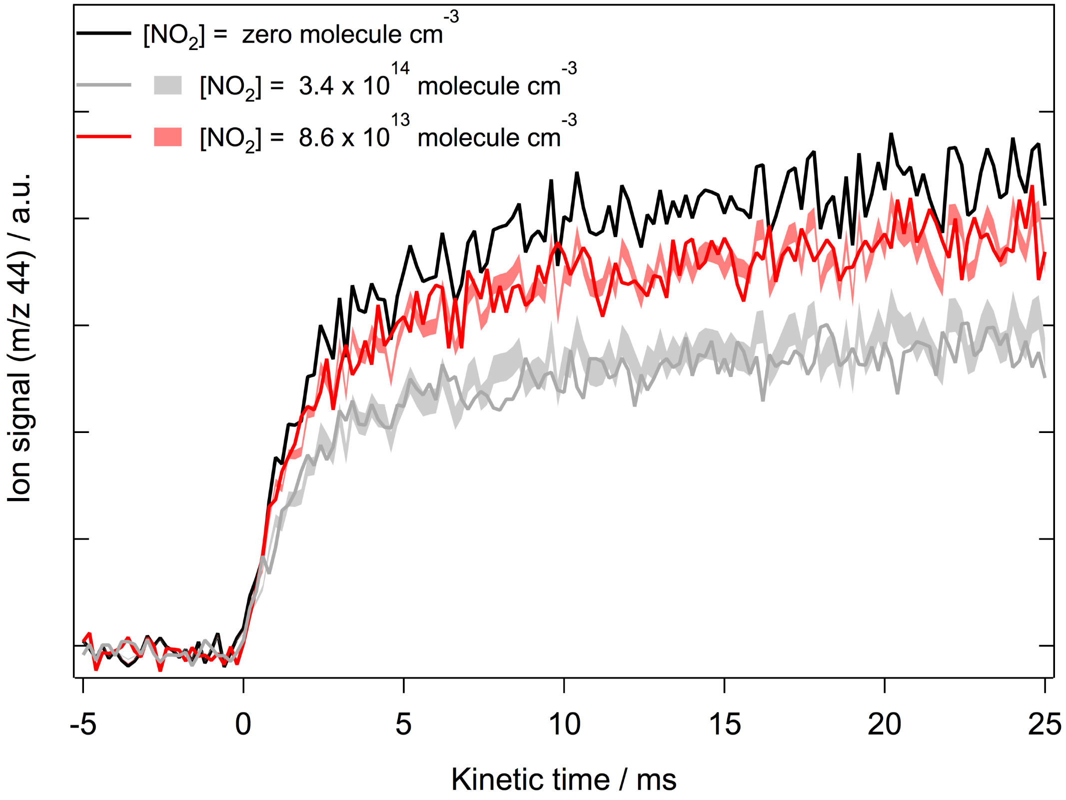


We estimate an **upper limit of ~30% NO_3 yield** based on acetaldehyde signal

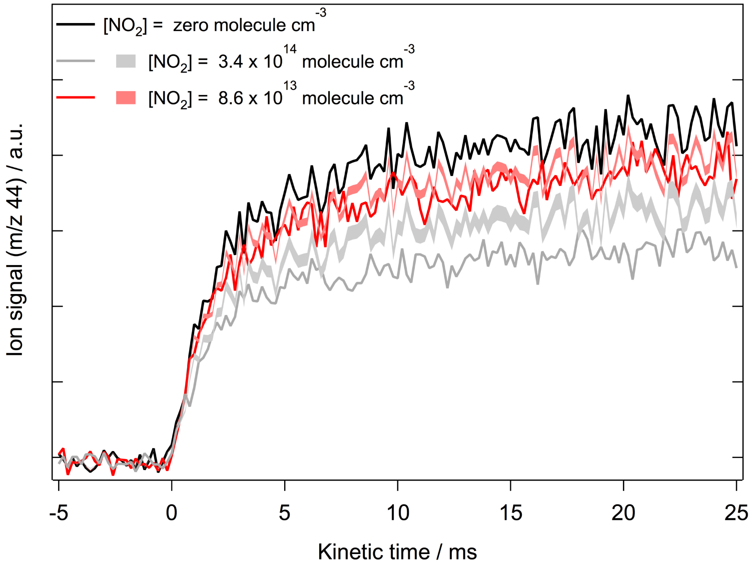
0 % *R1a*



30 % *R1a*



50 % *R1a*



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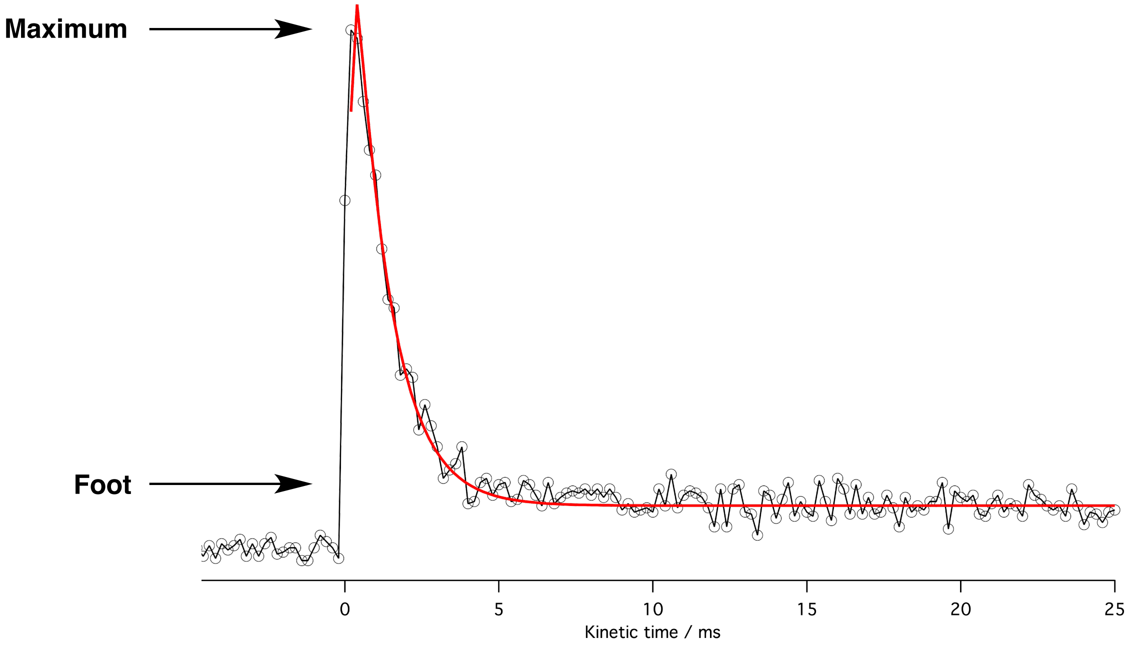
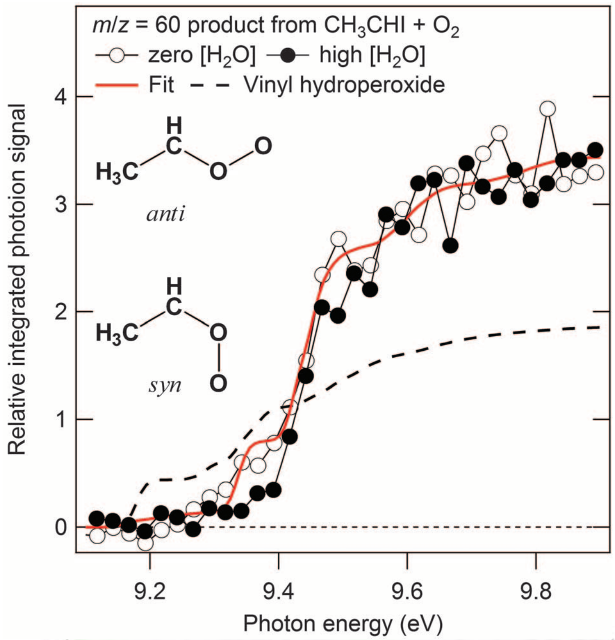
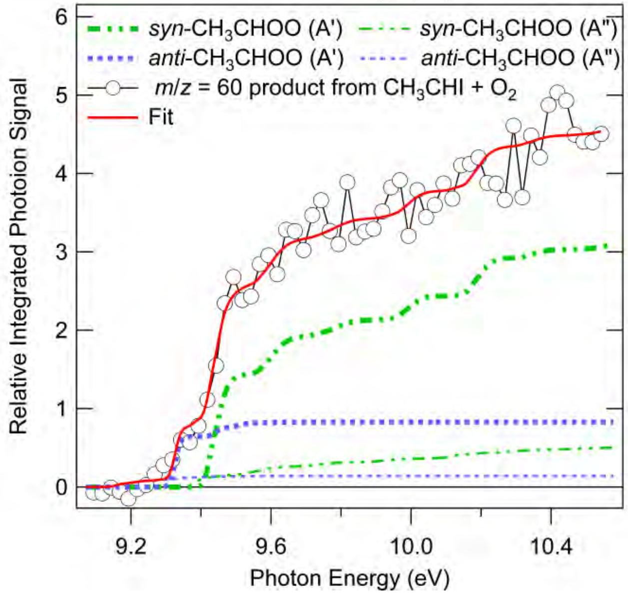
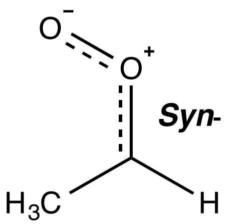
Y-axis offset on Criegee Kinetic Trace due to Isomerization



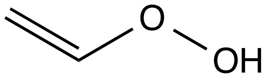




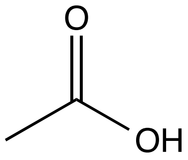
Reproduced from Taatjes et al., Science, 2013.



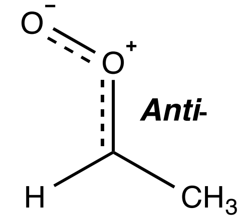
Syn-



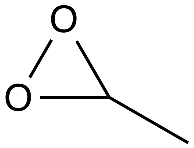
Vinylhydroperoxide
9.18 eV



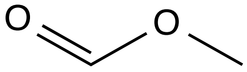
Acetic acid
10.7eV



Anti-



Methyldioxirane
10.36 eV



Methyl formate
10.8 eV

C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.

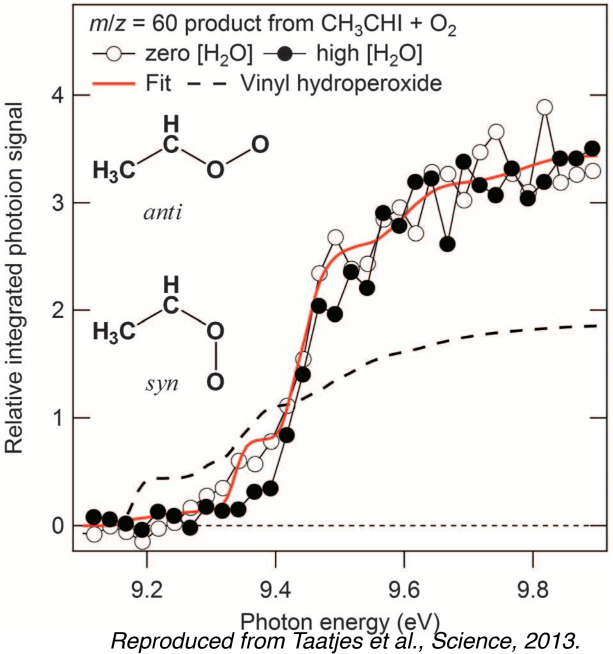
No evidence of NO_2-facilitated isomerization

Isomerization of Criegee Intermediates to various isomers would result in a **change in the kinetic profile** if a suitable photon energy is used for ionization.

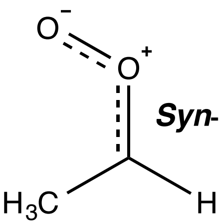
Evidence for **NO_2 (and SO_2)-assisted isomerization of acetone oxide** observed by Chhantyal-Pun *et al.*

Manifested in the long-time signal height **(foot) of m/z 74 increasing relative to the peak maximum as *f*[NO_2].**

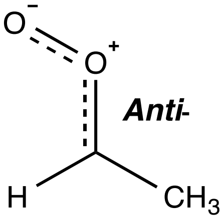
Isomerization products characterized as 2-hydroperoxypropene and methyldioxirane



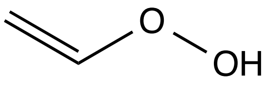
Reproduced from Taatjes et al., Science, 2013.



Syn-



Anti-



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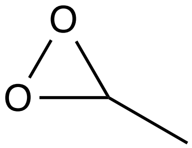

Methyldioxirane
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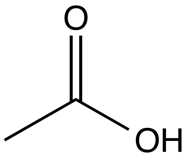

Acetic acid
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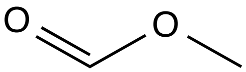

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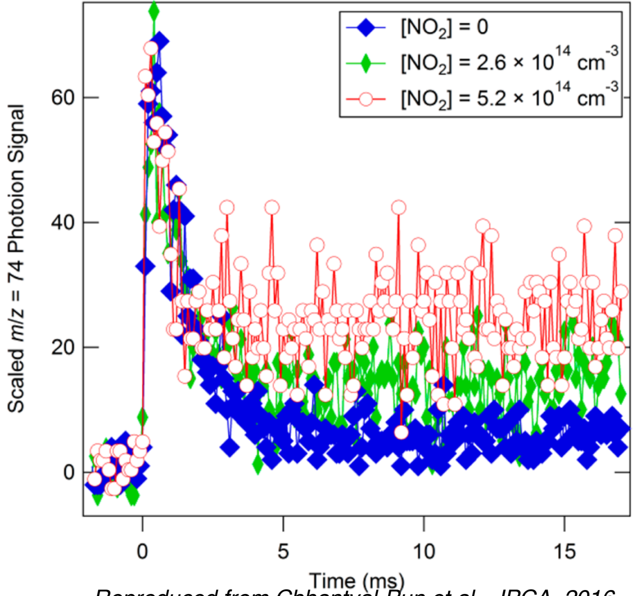

Reproduced from Chhantyal-Pun et al., JPCA, 2016

C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.
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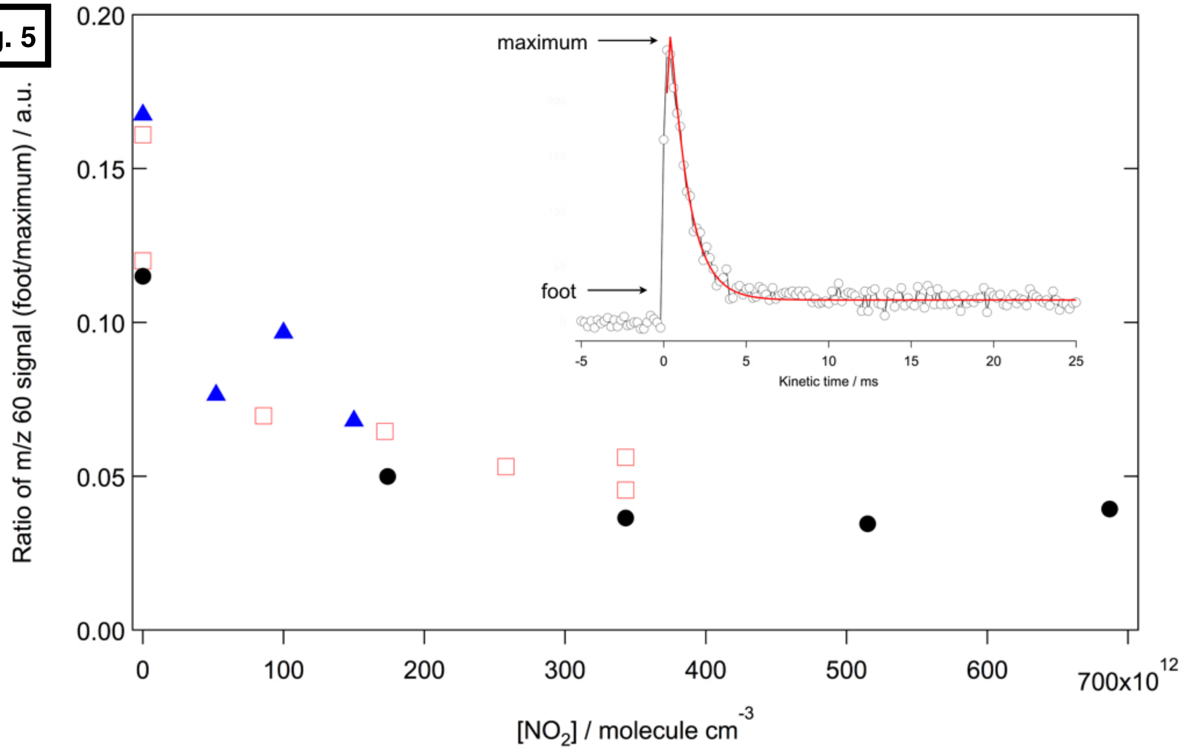
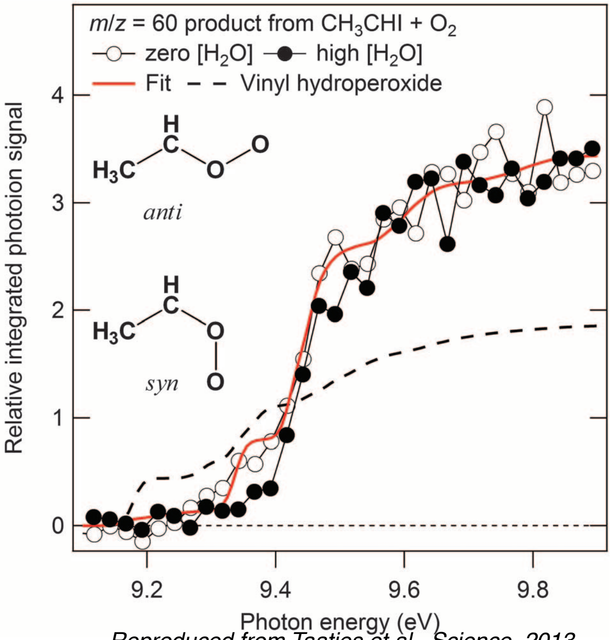
No evidence of NO_2-facilitated isomerization

Fig. 5





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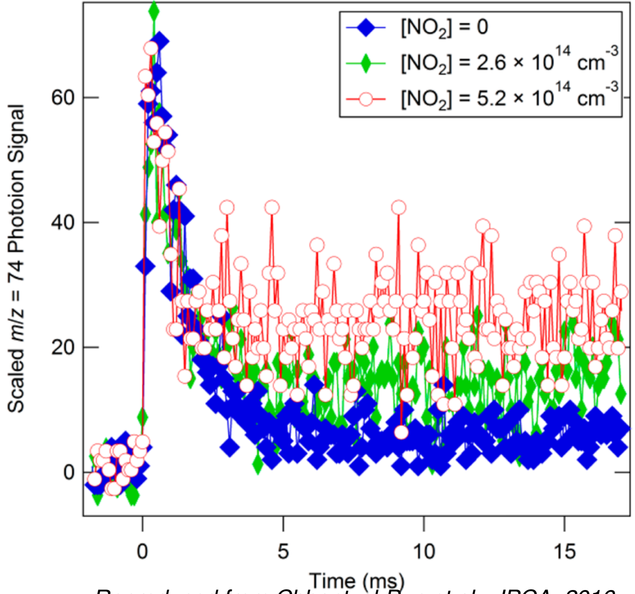

Reproduced from Chhantyal-Pun et al., JPCA, 2016

At 10.5 eV, we observe contributions to m/z 60 from *anti*- and *syn*-acetaldehyde oxide as well as **vinyl hydroperoxide and methyl dioxirane.**

A **positive** slope on a plot of (foot/maximum) *vs.* [NO_2] would be indicative of **NO_2-facilitated isomerization.**

Ratio of m/z 60 (foot/maximum) **decreases** as *f*[NO_2] over the entire pressure range (4-40 Torr).

No evidence of substantial NO_2-facilitated isomerization for acetaldehyde oxide.

C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.
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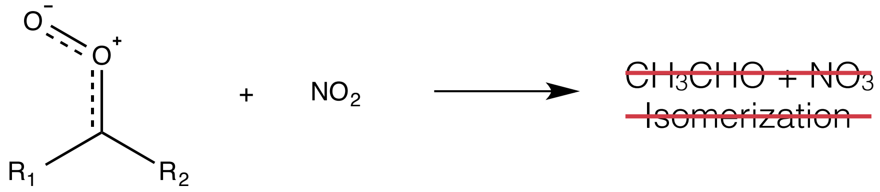
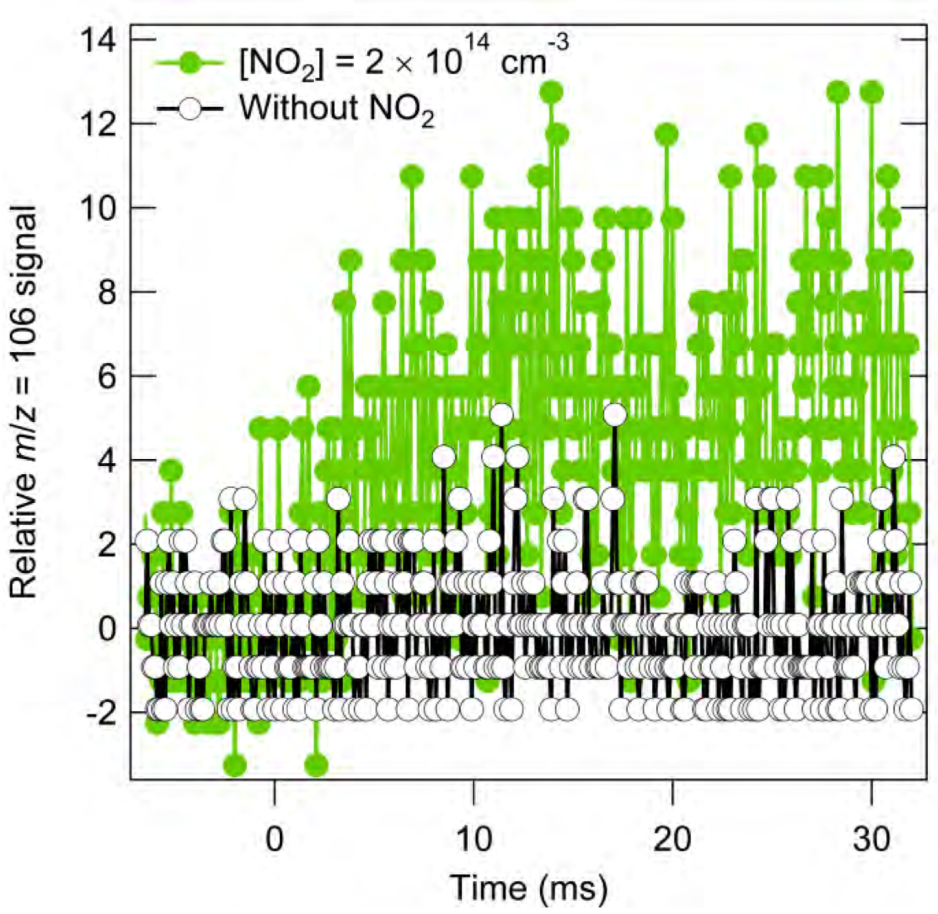
Products of Acetaldehyde Oxide + NO_2 : Adduct



m/z 106 observed in previous experiments by Taatjes *et al.* → **Adduct Formation ?**

Further experiments were required to ascertain it’s origin.



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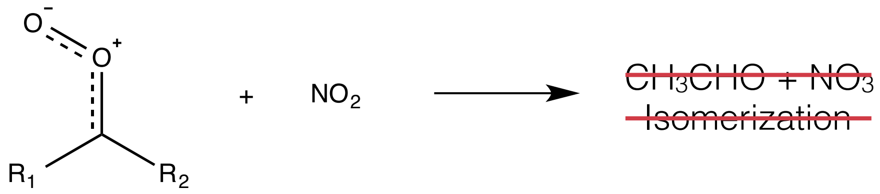

~~$CH_3CHO + NO_3$~~

~~Isomerization~~

m/z 106 observed in previous experiments by Taatjes *et al.* → **Adduct Formation ?**

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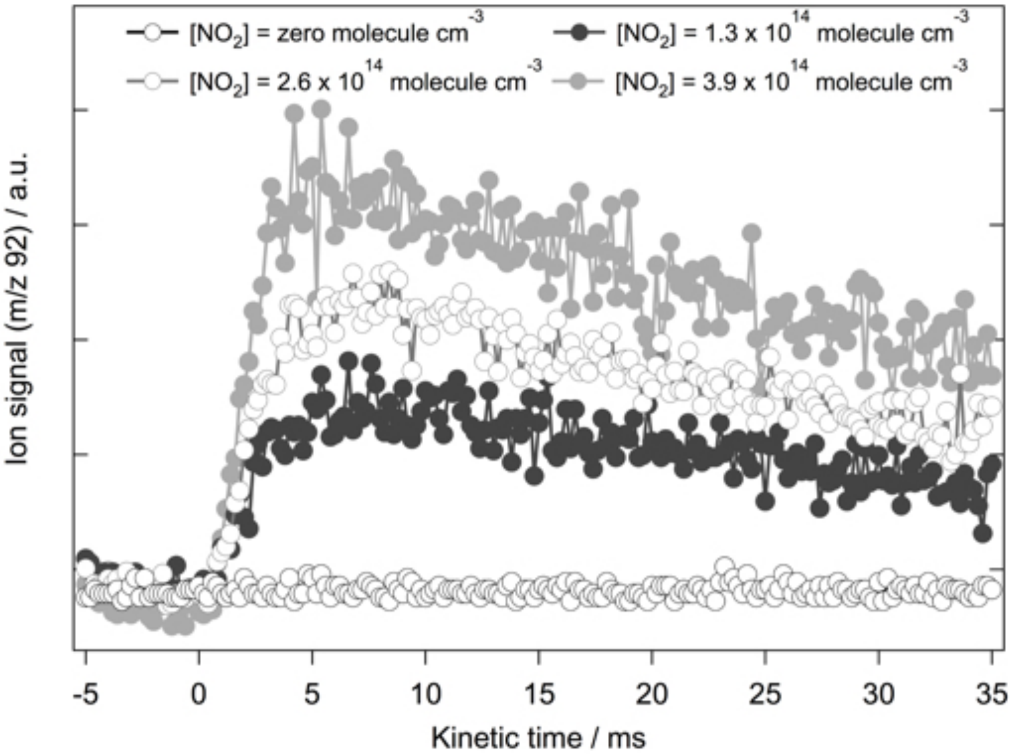
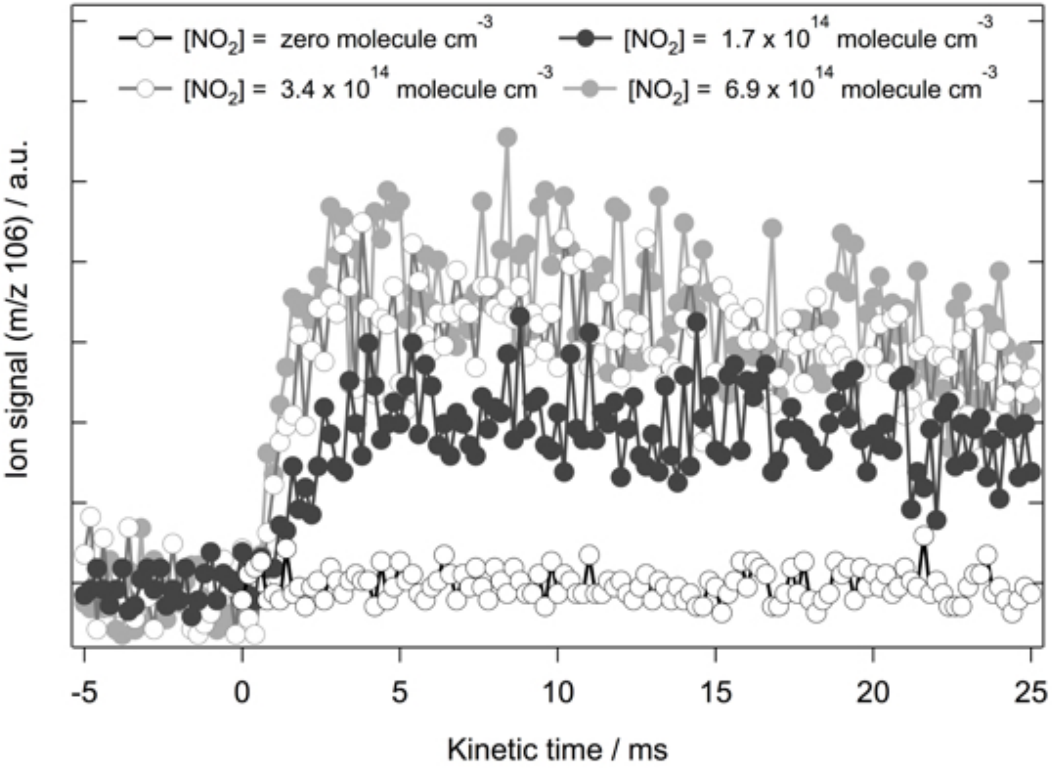
$[NO_2]$- and time-dependent signals observed at corresponding nominal m/z of adducts in **formaldehyde- and acetaldehyde-oxide systems**.

Formaldehyde oxide + NO_2, 30 Torr, 300 K, 10.5 eV



Acetaldehyde oxide + NO_2, 40 Torr, 300 K, 10.5 eV



C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.
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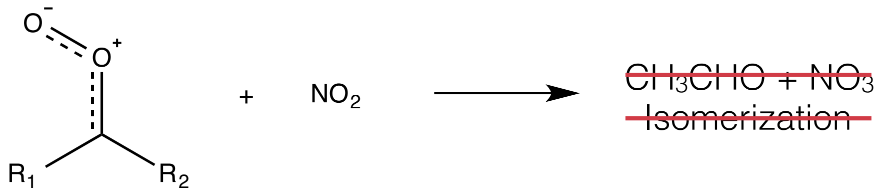
Products of Acetaldehyde Oxide + NO_2 : Adduct



~~$CH_3CHO + NO_3$~~

~~Isomerization~~

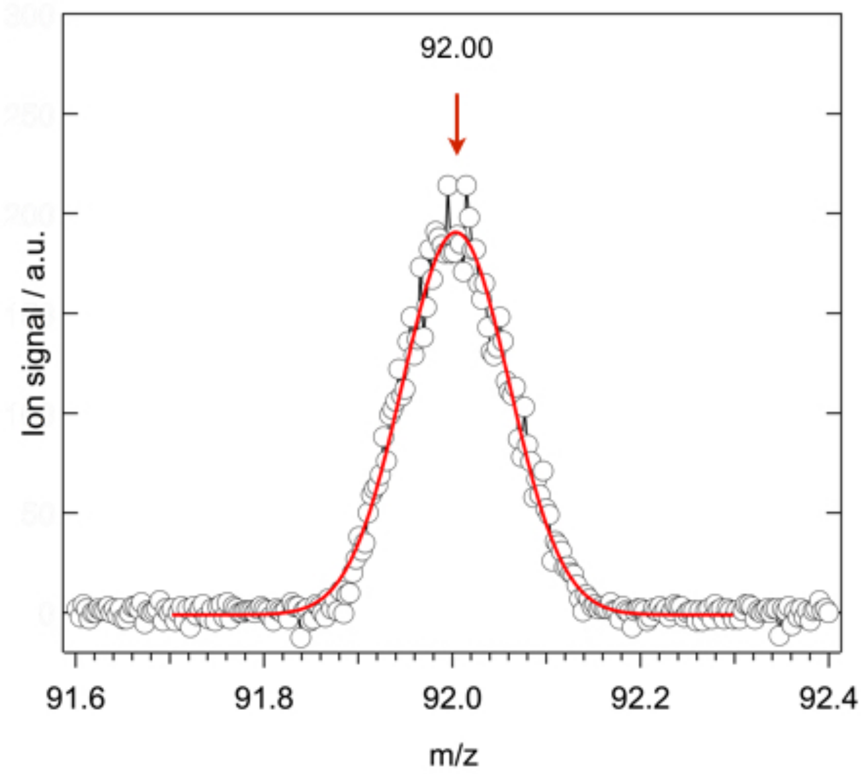
m/z 106 observed in previous experiments by Taatjes *et al.* → **Adduct Formation ?**

Further experiments were required to ascertain it’s origin.

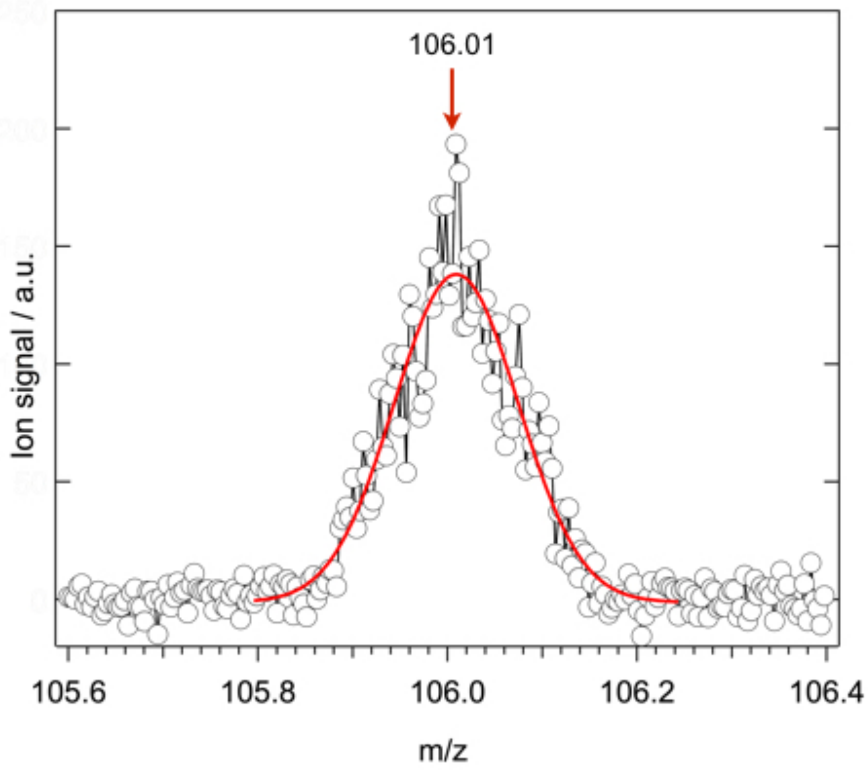
[NO_2]- and time-dependent signals observed at corresponding nominal m/z of adducts in **formaldehyde- and acetaldehyde-oxide systems**.

Exact m/z correspond to **CH_2O_4N and $C_2H_4O_4N$** respectively
→ **Consistent with adduct.**

Formaldehyde oxide + NO_2, 30 Torr, 300 K, 10.5 eV

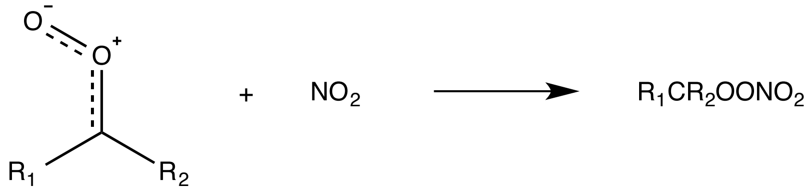


Acetaldehyde oxide + NO_2, 40 Torr, 300 K, 10.5 eV



C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.
R. L. Caravan, M. A. H. H. Khan, B. Rotavera, E. Papajak, I. Antonov, M.-W. Chen, K. Au, W. Chao, D. L. Osborn, J.-J. M. Lin, C. J. Percival, D. E. Shallcross and C. A. Taatjes, *Faraday discussions*, 2017, Accepted.

Products of Acetaldehyde Oxide + NO_2 : Adduct

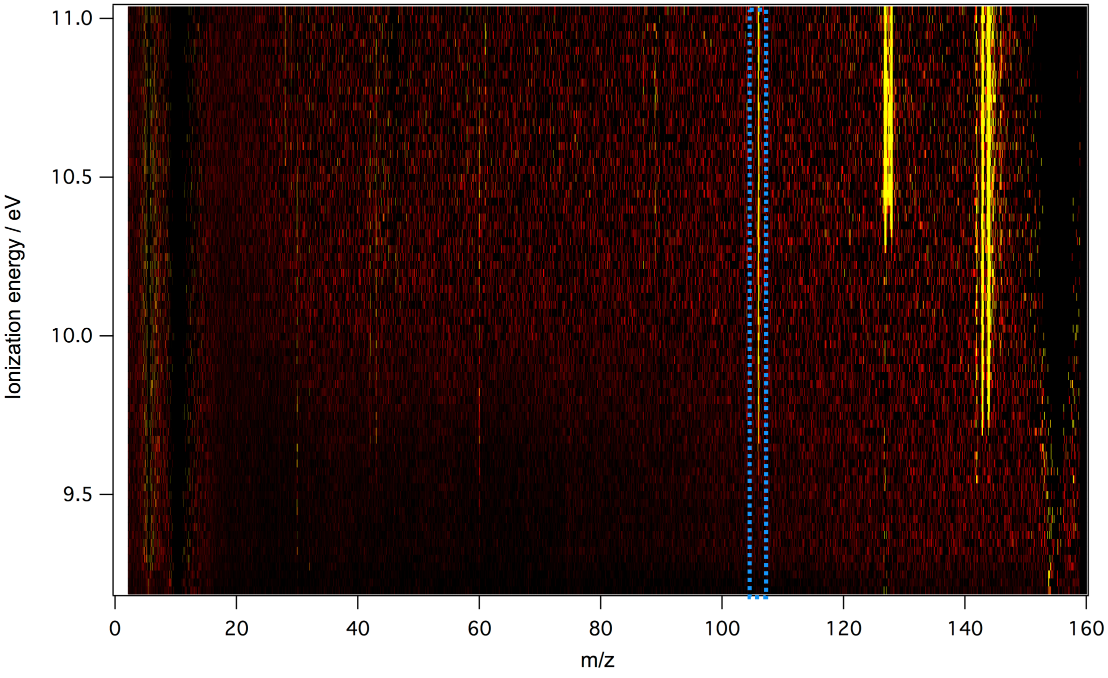


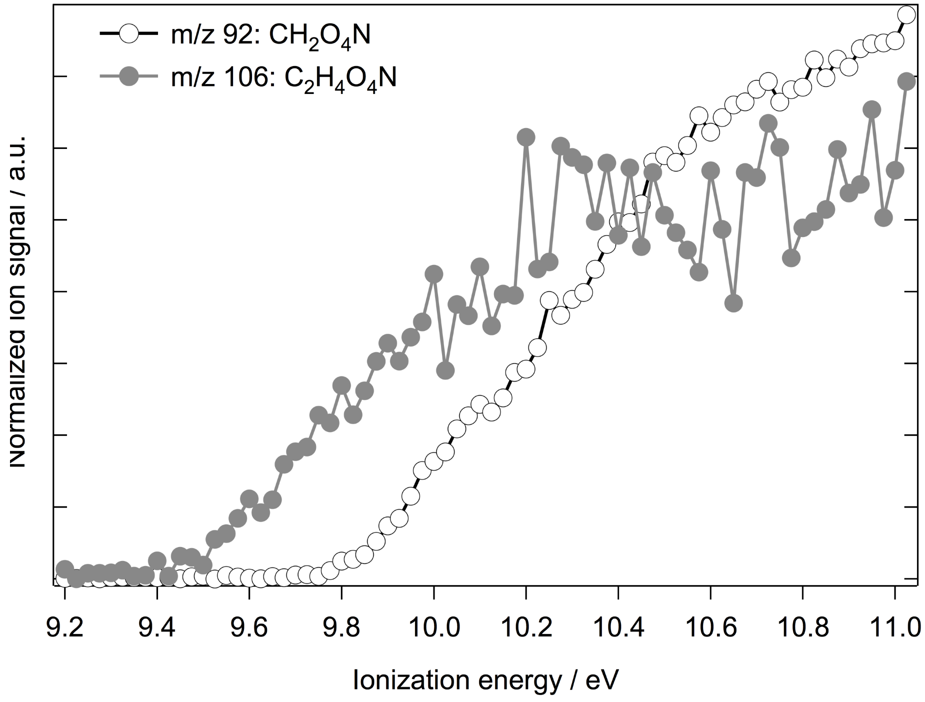
What is the **structure** of the adduct ?

Photoionization energy spectra of the corresponding m/z obtained from the 3D dataset recorded from the reactions of formaldehyde- and acetaldehyde-oxide with NO_2.

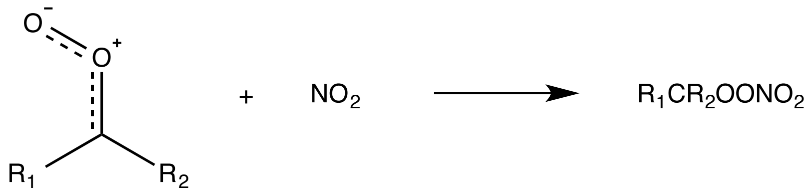
No bottled standards with which we can compare these to: **Calculations required.**

EX: Photoionization energy spectrum of m/z over a given temporal range





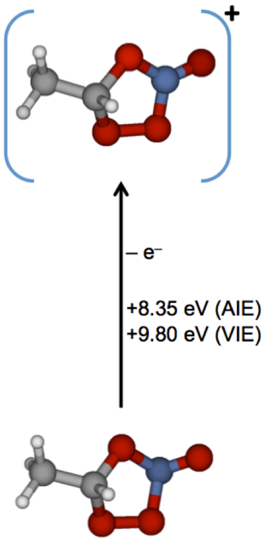
Products of Acetaldehyde Oxide + NO_2 : Adduct



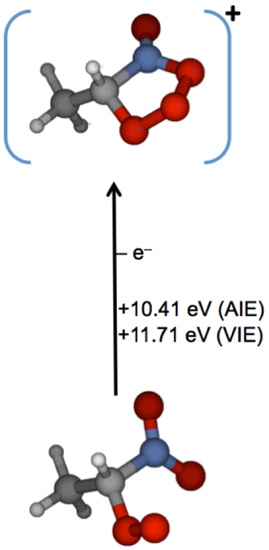
Stationary point calculations and adiabatic ionization energy calculations performed at the ωB97XD/6-31+G(d) level of density functional theory **(Papajak)**.

Similar onset energy calculated for **RCR(ONO)OO structure** calculated but **dissociative ionization predicted - in conflict with current observations** of parent mass.

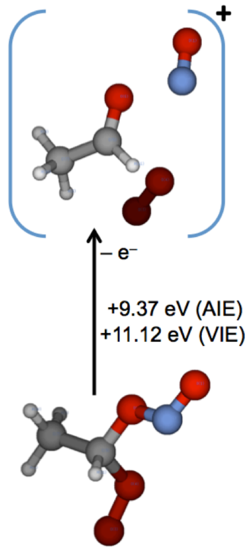
Further work needed to establish structure.



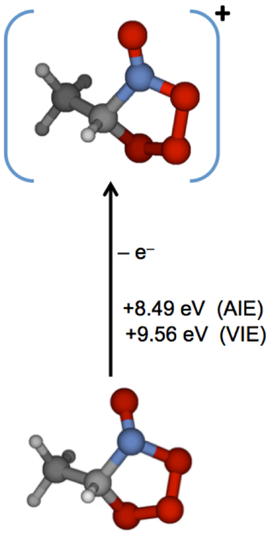
Isomer #1
H(0K) = 23.55 kcal/mol



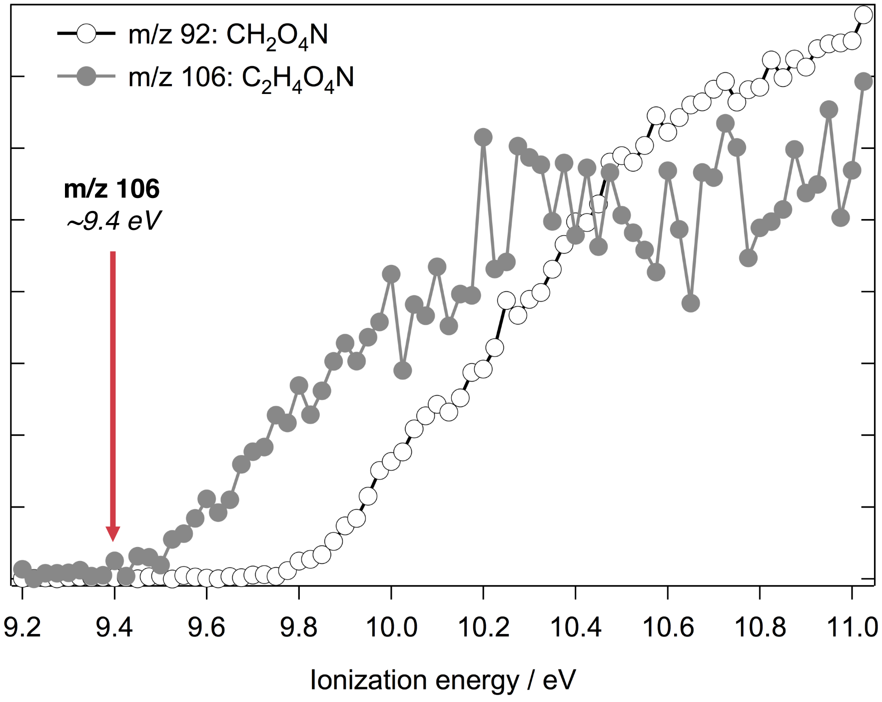
Isomer #2
H(0K) = 4.68 kcal/mol



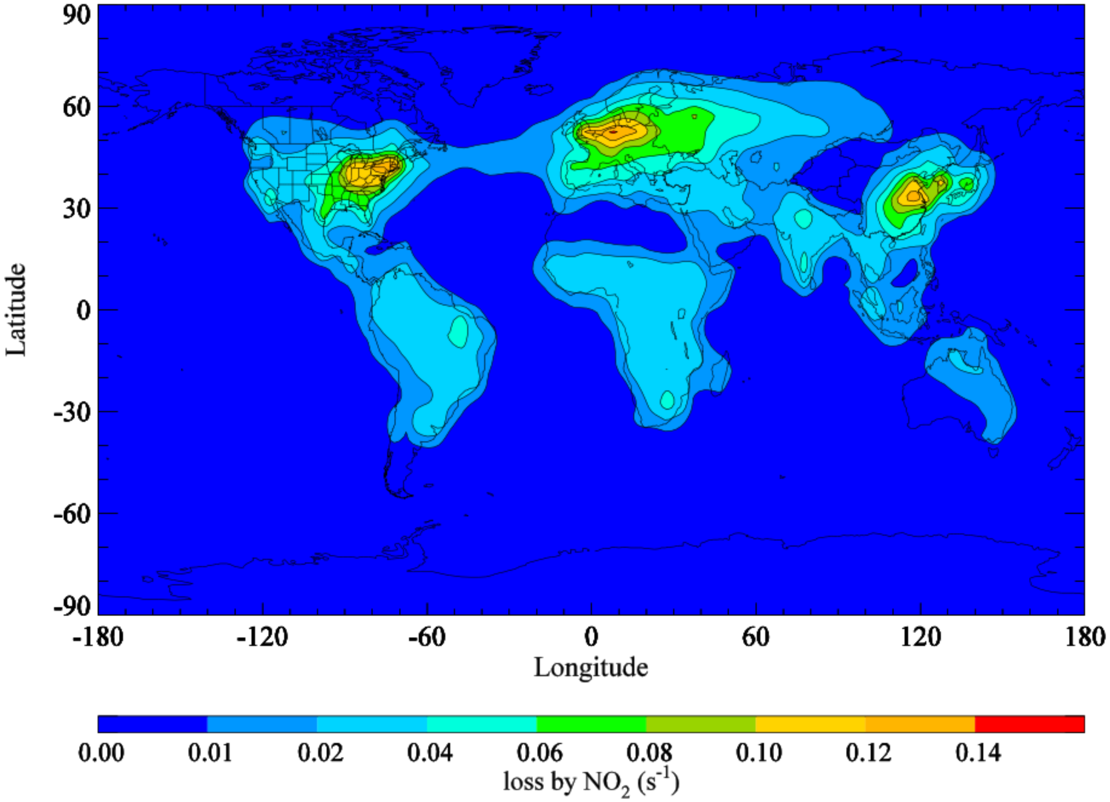
Isomer #3
H(0K) = 0.00 kcal/mol



Isomer #4
H(0K) = 48.95 kcal/mol



Atmospheric impact



Impact of Criegee + NO_2 measured rate coefficient on global atmospheric Criegee Intermediate loss assessed through the global chemistry transport model STOCHEM-CRI **(Khan and Shallcross)**.

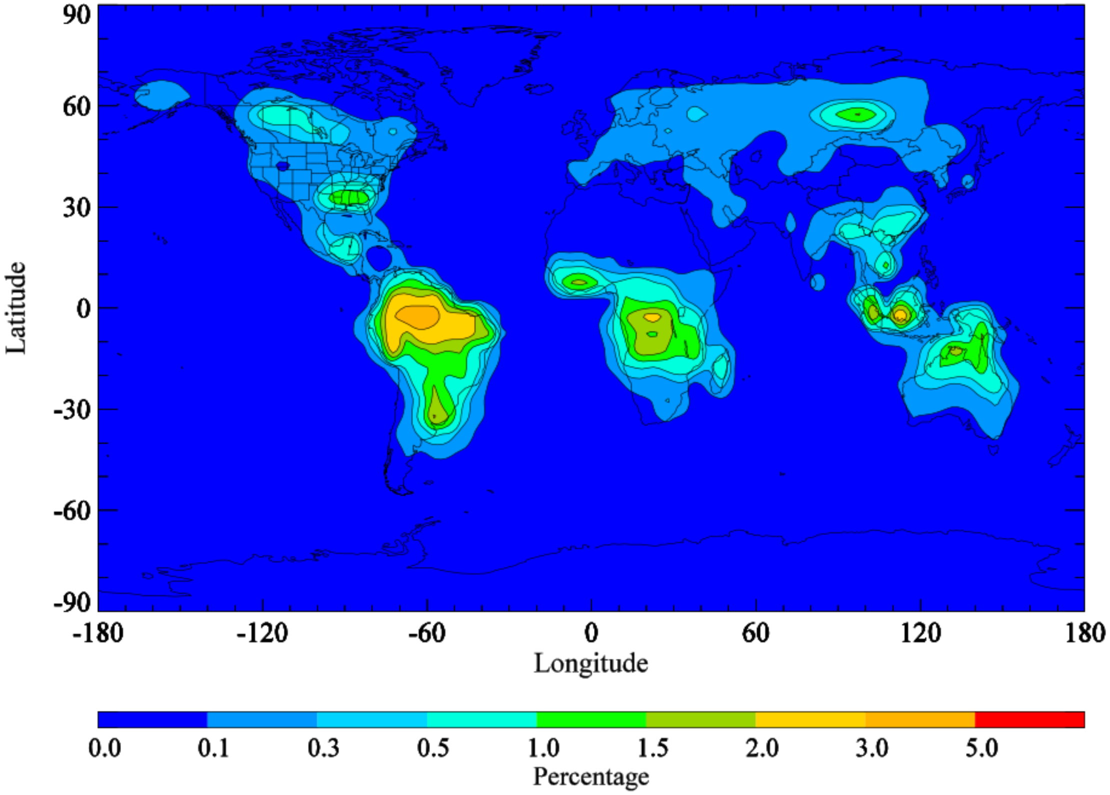
Unimolecular loss (fixed at 100 s^{-1} for all Criegees), reaction with water vapor, and fast reaction with the water dimer (for formaldehyde oxide) accounted for.

Loss via reaction with NO_2 accounts for <0.15 s^{-1}: Peak loss concentrated around polluted areas in particular large cities in the northern hemisphere.

Unimolecular loss represents a much greater loss still.

S. R. Utembe, M. C. Cooke, A. T. Archibald, M. E. Jenkin, R. G. Derwent and D. E. Shallcross, *Atmospheric Environment*, 2010, 44, 1609-1622., S. R. Utembe, M. C. Cooke, A. T. Archibald, D. E. Shallcross, R. G. Derwent and M. E. Jenkin, *Atmospheric environment*, 2011, 45, 1604-1614., S. R. Utembe, L. A. Watson, D. E. Shallcross and M. E. Jenkin, *Atmospheric Environment*, 2009, 43, 1982-1990., L. A. Watson, D. E. Shallcross, S. R. Utembe and M. E. Jenkin, *Atmospheric Environment*, 2008, 42, 7196-7204., M. E. Jenkin, L. A. Watson, S. R. Utembe and D. E. Shallcross, *Atmospheric Environment*, 2008, 42, 7185-7195., R. Derwent, D. Stevenson, R. Doherty, W. Collins and M. Sanderson, *Atmospheric Environment*, 2008, 42, 7412-7422., W. Collins, D. S. Stevenson, C. Johnson and R. Derwent, *Journal of Atmospheric Chemistry*, 1997, 26, 223-274., R. L. Caravan, M. A. H. H. Khan, B. Rotavera, E. Papajak, I. Antonov, M.-W. Chen, K. Au, W. Chao, D. L. Osborn, J.-J. M. Lin, C. J. Percival, D. E. Shallcross and C. A. Taatjes, *Faraday discussions*, 2017, Accepted.

Atmospheric impact



Impact on NO_3 production from this reaction assuming 100 % yield of NO3 + aldehyde/ketone also assessed through the global chemistry transport model STOCHEM-CRI (Khan and Shallcross)

Percentage increase in NO_3 production compared to the principal production pathway (O_3 + NO_2) is **found to be < 4 %).**

Accounting for the revised upper limit of ~ 30 %, this effect will be lessened.

Atmospheric fate and impact of the adduct needs to be understood

S. R. Utembe, M. C. Cooke, A. T. Archibald, M. E. Jenkin, R. G. Derwent and D. E. Shallcross, *Atmospheric Environment*, 2010, 44, 1609-1622., S. R. Utembe, M. C. Cooke, A. T. Archibald, D. E. Shallcross, R. G. Derwent and M. E. Jenkin, *Atmospheric environment*, 2011, 45, 1604-1614., S. R. Utembe, L. A. Watson, D. E. Shallcross and M. E. Jenkin, *Atmospheric Environment*, 2009, 43, 1982-1990., L. A. Watson, D. E. Shallcross, S. R. Utembe and M. E. Jenkin, *Atmospheric Environment*, 2008, 42, 7196-7204., M. E. Jenkin, L. A. Watson, S. R. Utembe and D. E. Shallcross, *Atmospheric Environment*, 2008, 42, 7185-7195., R. Derwent, D. Stevenson, R. Doherty, W. Collins and M. Sanderson, *Atmospheric Environment*, 2008, 42, 7412-7422., W. Collins, D. S. Stevenson, C. Johnson and R. Derwent, *Journal of Atmospheric Chemistry*, 1997, 26, 223-274., R. L. Caravan, M. A. H. H. Khan, B. Rotavera, E. Papajak, I. Antonov, M.-W. Chen, K. Au, W. Chao, D. L. Osborn, J.-J. M. Lin, C. J. Percival, D. E. Shallcross and C. A. Taatjes, *Faraday discussions*, 2017, Accepted.

Conclusions & Remaining Questions

- Reaction of formaldehyde oxide and acetaldehyde oxide Criegee intermediates with NO_2 studied via MPIMS interfaced with tunable VUV radiation.
- Kinetics for acetaldehyde oxide + NO_2 obtained at 20 and 40 Torr - Independent of pressure and in line with previous lower pressure values.
- NO_3 was not detected from the reaction. Based on the acetaldehyde signal as $f[NO_2]$:**Upper limit for the NO_3 yield was placed at ~ 30 %.**
- **No evidence for [NO_2]-facilitated isomerization of acetaldehyde oxide**, as observed in acetone oxide + NO_2, SO_2.
- Time and [NO_2]-dependent signal observed at the m/z of the **Criegee-NO_2 adduct** for both formaldehyde oxide and acetaldehyde oxide systems.
- As little evidence for other products, **adduct thought to be the major reaction product (> 70 %)**.
- Structure of adducts remains unclear, further calculations underway.
- **Investigations of the atmospheric fate of the adduct are important**: If it has decomposition products do they effect NOx/NOy chemistry ?

R. Chhantyal-Pun, O. Welz, J. D. Savee, A. J. Eskola, E. P. Lee, L. Blacker, H. R. Hill, M. Ashcroft, M. A. H. Khan, G. C. Lloyd-Jones, L. Evans, B. Rotavera, H. Huang, D. L. Osborn, D. K. W. Mok, J. M. Dyke, D. E. Shallcross, C. J. Percival, A. J. Orr-Ewing and C. A. Taatjes, *The Journal of Physical Chemistry A*, 2016.

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Ming-Wei Chen
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David Osborn
Craig Taatjes
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Model for CH_3CHO signal

From measured bimolecular rate coefficient, we can calculate the % loss of Criegee due to reaction with NO_2 at a given $[NO_2]$.

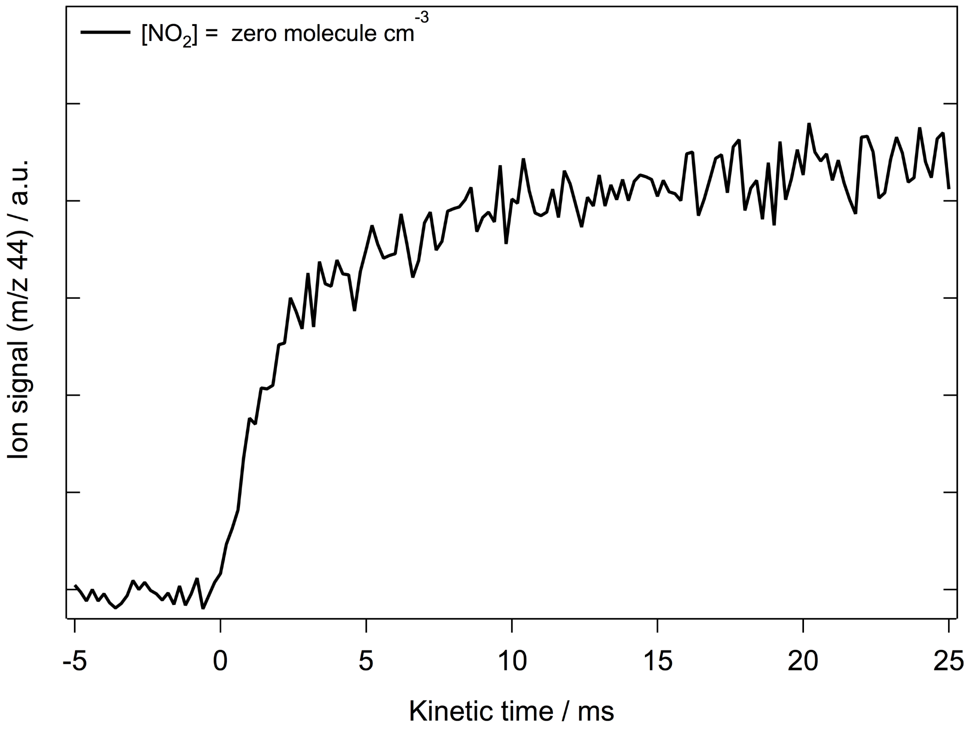
% CI Loss due to reaction = $(k'_{NO2}/(k'_{NO2}+k'_{intercept})) \times 100$.

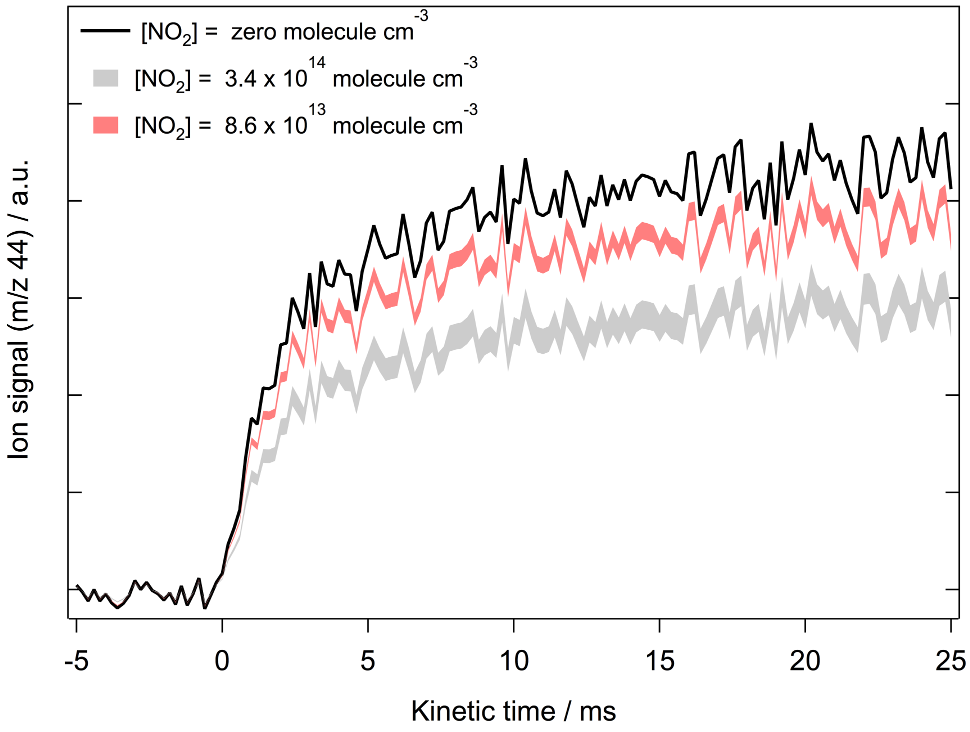
The anticipated signal can be calculated by the following:

$\text{Signal}_{(NO2)} = \text{Signal}_{(no\ NO2)} \times (100\% - (\%\ \text{CI loss due to reaction} \times \text{yield}))$

Using the upper (2.0×10^{-12} molecule cm^{-3} s^{-1}) and lower bound (1.4×10^{-12} molecule cm^{-3} s^{-1}) of the measured bimolecular rate coefficient for Criegee + NO_2, we can obtain the lower and upper bounds to the expected acetaldehyde signal.

The yield can be varied to simulate acetaldehyde signal profiles to compare with the measured experimental data.





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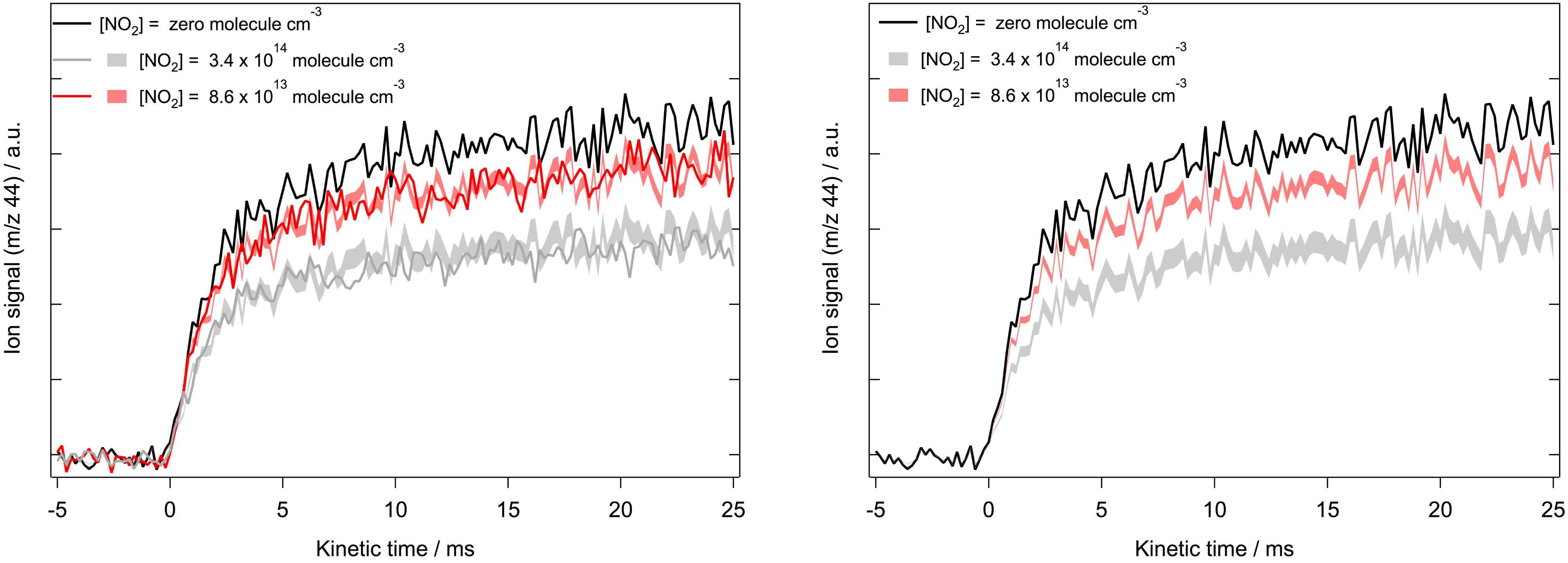
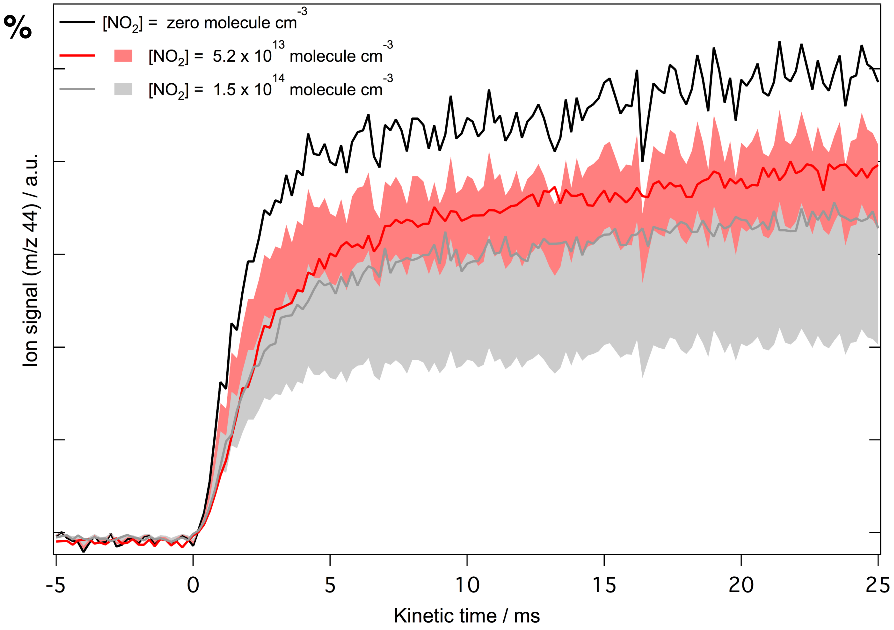
The yield can be varied to simulate acetaldehyde signal profiles to compare with the measured experimental data.

30 % CH_3CHO + NO_3



P-dependence of $CH_3CHO + NO_3$: 4 Torr

0 %



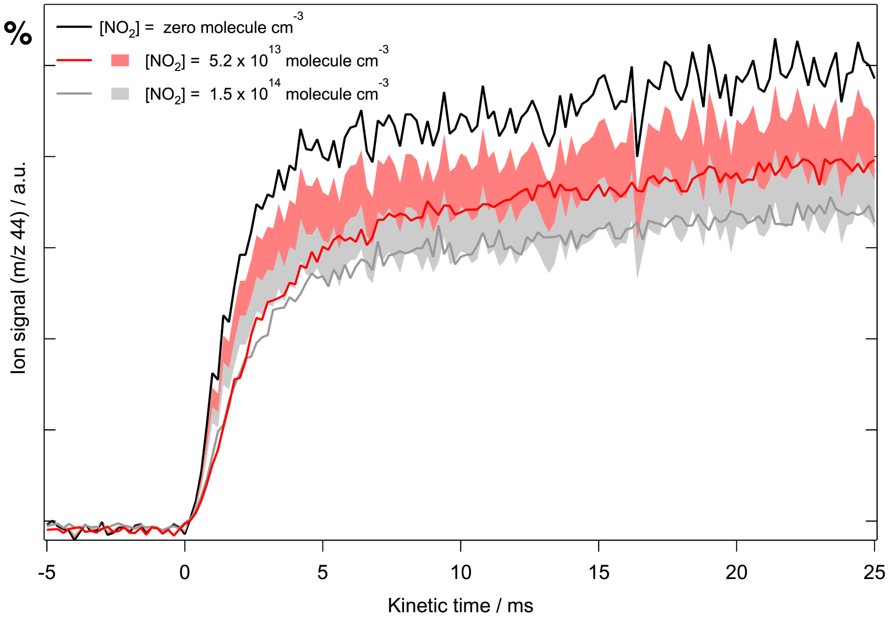
If the branching ratio of Criegee + NO_2 is pressure dependent, the bimolecular channel will have the highest yield at lower pressures.

The **yield of Criegee from RCR’I + O_2 is higher (68-99 % for C1 at 4 Torr N_2) at lower pressures**: Side chemistry from **RCR’IOO + I → RCR’O + IO + I is minimized**.

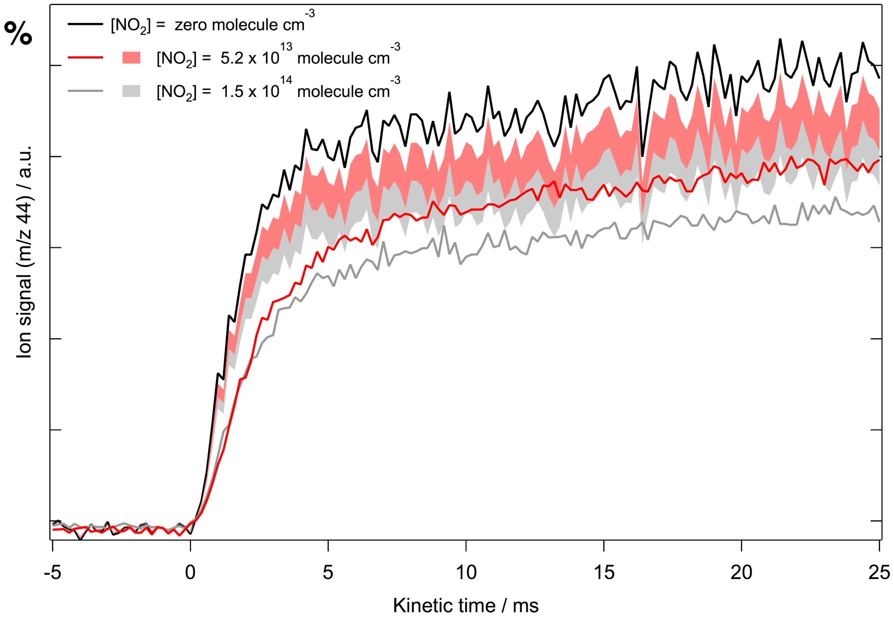
However, the **error on our bimolecular rate coefficient is larger** and so the error bands on the corresponding predicted acetaldehyde signals in the presence of NO_2 are larger.

~0-30 % yield simulates the experimental data well at 4 Torr.

30 %



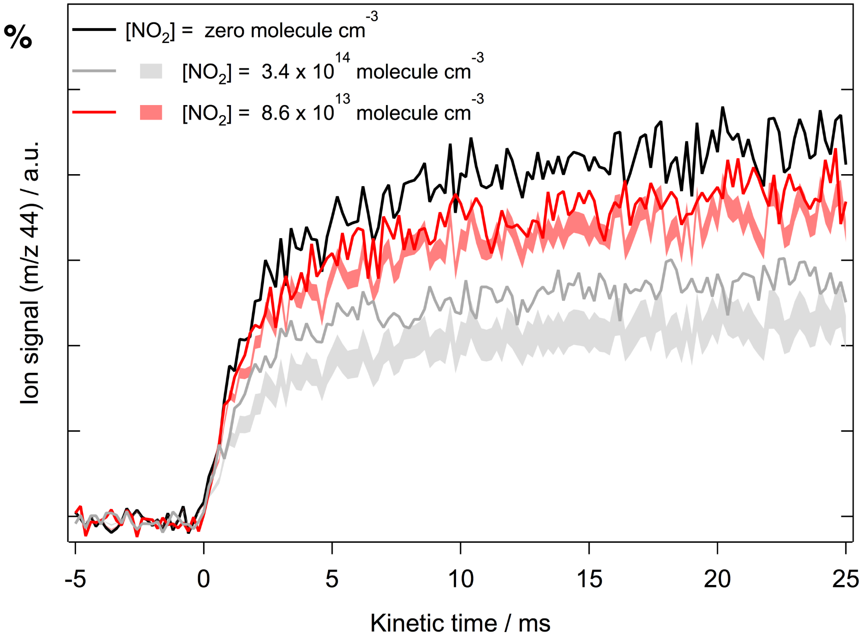
50 %



D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
T. J. Gravestock, M. A. Blitz, W. J. Bloss and D. E. Heard, *ChemPhysChem*, 2010, 11, 3928-3941.

P-dependence of $CH_3CHO + NO_3$: 20 Torr

0 %

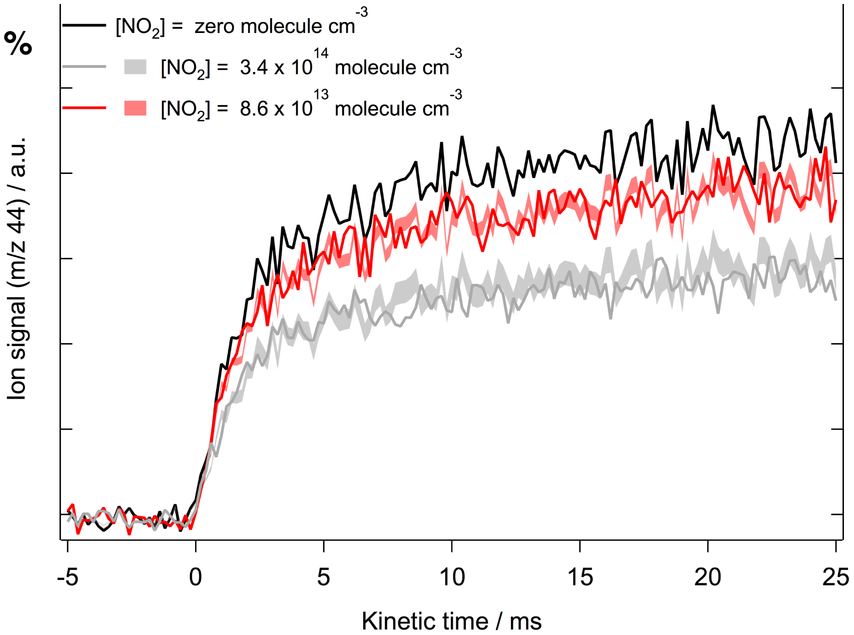


If the branching ratio of Criegee + NO_2 is pressure dependent, the bimolecular channel will have the highest yield at lower pressures.

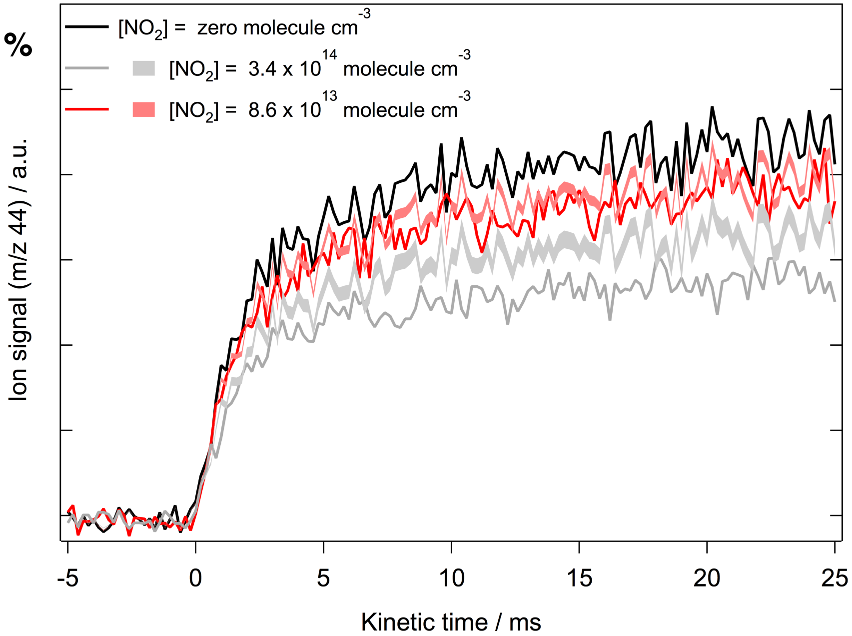
The **yield of Criegee from RCR'I + O_2 is slightly lower at 20 Torr (67-93 % for C1 at 20 Torr N_2) at lower pressures**: Side chemistry from **RCR'IOO + I → RCR'O + IO + I is more relevant, we do not attempt to account for this.**

~**30 % yield** simulates the experimental data well at 20 Torr.

30 %



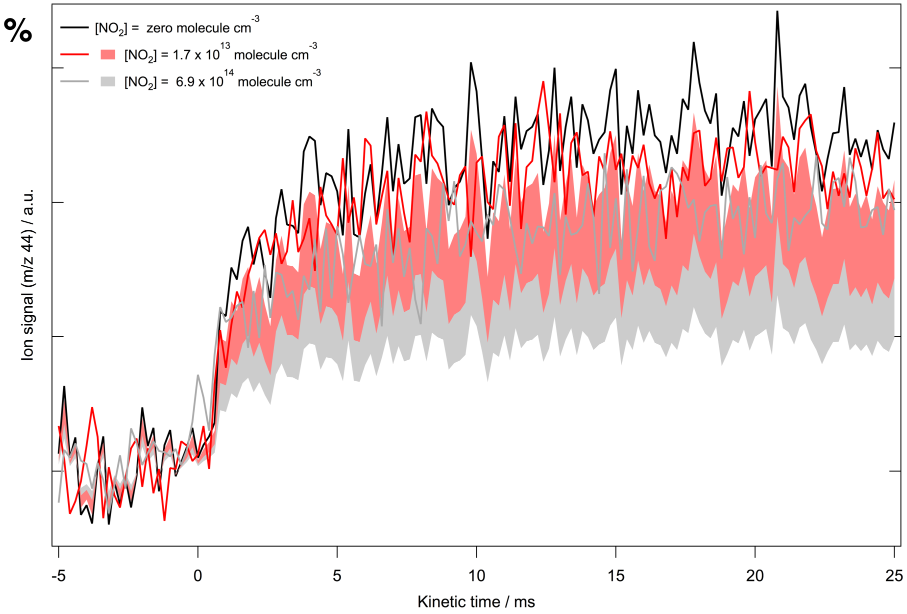
50 %



D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
T. J. Gravestock, M. A. Blitz, W. J. Bloss and D. E. Heard, *ChemPhysChem*, 2010, 11, 3928-3941.

P-dependence of $CH_3CHO + NO_3$: 40 Torr

0 %

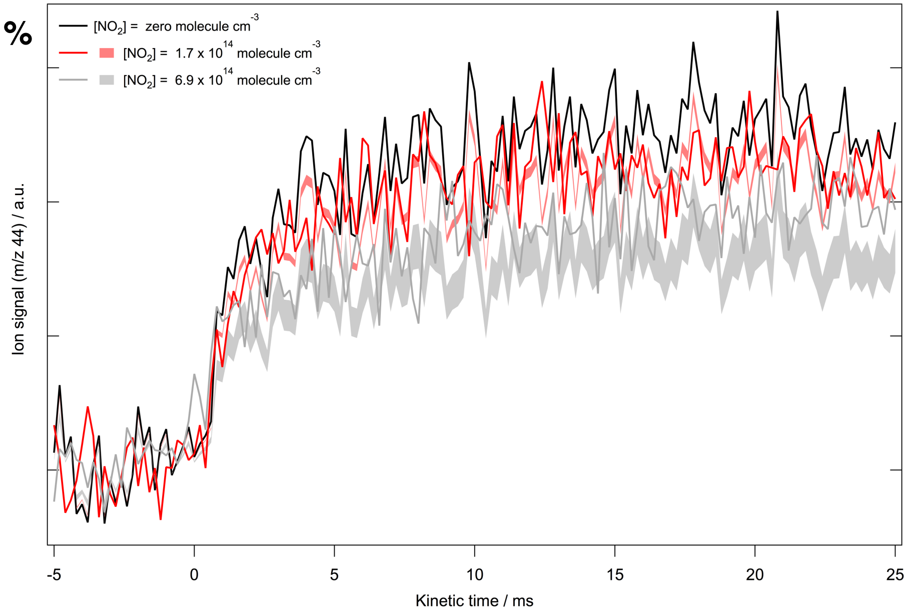


If the branching ratio of Criegee + NO_2 is pressure dependent, the bimolecular channel will have the highest yield at lower pressures.

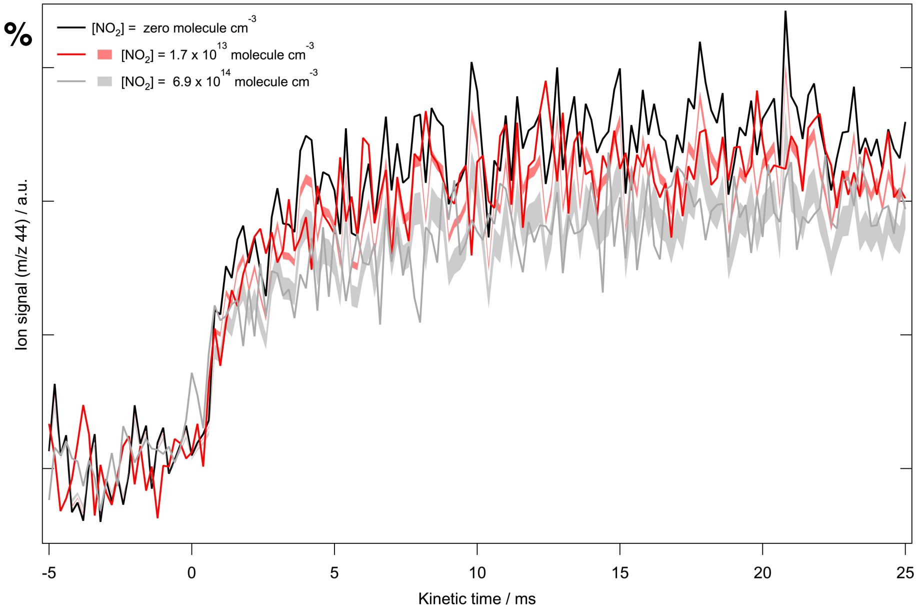
The **yield of Criegee from RCR'I + O_2 is slightly lower at 20 Torr (64-86 % for C1 at 40 Torr N_2) at lower pressures**: Side chemistry from **RCR'IOO + I → RCR'O + IO + I is more relevant, we do not attempt to account for this.**

~**30-50 % yield** simulates the experimental data well at 40 Torr.

30 %



50 %



D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
T. J. Gravestock, M. A. Blitz, W. J. Bloss and D. E. Heard, *ChemPhysChem*, 2010, 11, 3928-3941.

Sources of CH_3CHO

$$CH_3CHI + O_2 \longrightarrow \left.\begin{array}{l} CH_3CHOO + I \\ CH_3CHIOO \end{array}\right\} \textit{Pressure dependent}$$

1. Reactions of Criegee

$CH_3CHOO + I \longrightarrow CH_3CHO + IO$ — *$k \sim 3.5 \times 10^{-11}$ molecule^{-1} cm^3 s^{-1} (estimated for C1)*

$CH_3CHOO + NO_2 \longrightarrow CH_3CHO + NO_3$ — *$k = 2.0 \times 10^{-12}$ molecule^{-1} cm^3 s^{-1}*

2. Reactions of iodoalkylperoxy

$CH_3CHIOO + I \longrightarrow CH_3CHO + IO + I$ — *$k \sim 3.5 \times 10^{-11}$ molecule^{-1} cm^3 s^{-1} (for C1)*

$CH_3CHIOO + CH_3CHIOO \longrightarrow 2CH_3CHIO + O_2$ — *$k \sim 9 \times 10^{-11}$ molecule^{-1} cm^3 s^{-1} (for C1)*

$CH_3CHIO \longrightarrow CH_3CHO + I$ — *Fast ! (for C1)*

Not accounted for in our acetaldehyde model, will contribute more at higher pressures.

D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.
T. J. Gravestock, M. A. Blitz, W. J. Bloss and D. E. Heard, *ChemPhysChem*, 2010, 11, 3928-3941.

Sinks of CH_3CHIOO

$$CH_3CHI + O_2 \longrightarrow \left.\begin{array}{l} CH_3CHOO + I \\ CH_3CHIOO \end{array}\right\} \textit{Pressure dependent}$$

$CH_3CHIOO + I \longrightarrow CH_3CHO + IO + I$ *$k \sim 3.5 \times 10^{-11}$ molecule^{-1} cm^{3} s^{-1} (for C1)*

$CH_3CHIOO + CH_3CHIOO \longrightarrow 2CH_3CHIO + O_2$ *$k \sim 9 \times 10^{-11}$ molecule^{-1} cm^{3} s^{-1} (for C1)*

$CH_3CHIO \longrightarrow CH_3CHO + I$ *Fast ! (for C1)*

$CH_3CHIOO + NO_2 \longrightarrow$ Products *$k \sim 1\text{-}2 \times 10^{-12}$ molecule^{-1} cm^{3} s^{-1} (estimated, based on Huang et al.)*

$[NO_2] \sim 10^{14}$ molecule^{-1} cm^{3} & $[I] \sim 10^{13}$ molecule^{-1} cm^{3}
Reactions of CH_3CHIOO these species will be competitive with one another

T. J. Gravestock, M. A. Blitz, W. J. Bloss and D. E. Heard, *ChemPhysChem*, 2010, 11, 3928-3941.
D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
M. Huang, N. Kline, T. A. Miller and R. Dawes, *The Journal of Physical Chemistry A*, 2017, 121, 98-112.

Ruling Out Side Chemistry in Adduct Formation

- **How do we know that the m/z 106 & m/z 92 signals are indeed from Criegee + NO_2 and not side chemistry ?**

$$\mathrm{RCR'OO + NO_2 \longrightarrow RCR'OONOO}$$

- Iodoalkylperoxy (RCR'IOO) occurs from the reaction of iodoalkyl (RCR'I) with O_2 and is in competition with Criegee formation.

$$\mathrm{RCR'I + O_2 \longrightarrow \begin{matrix} RCR'OO + I \\ RCR'IOO \end{matrix}}$$

- The yield of formaldehyde oxide from iodoalkyl + O_2 was investigated by Stone *et al.* At 4 Torr (N_2) 64-99 % is achieved, and at 40 Torr (N_2), 64-86 %.
- At **higher pressures the reactions of iodoalkylperoxy radicals will be more pertinent** as their yields are enhanced.
- Estimated rate coefficient for iodoalkylperoxy radicals with NO_2 by Stone *et al.* is on the order of the Criegee + NO_2 rate coefficient measured in this and previous work.

Kinetics alone cannot rule out their contribution to m/z 106 and m/z 92.

$$\mathrm{RCR'IOO + NO_2 \longrightarrow RCR'IOONO_2 \xrightarrow{\textit{VUV, DI}} \left[RCR'OONO_2\right]^{+} + I}$$

Calculate onset energy of the DI

$$\mathrm{RCR'IOO + NO_2 \longrightarrow RCR'OONO_2 + I}$$

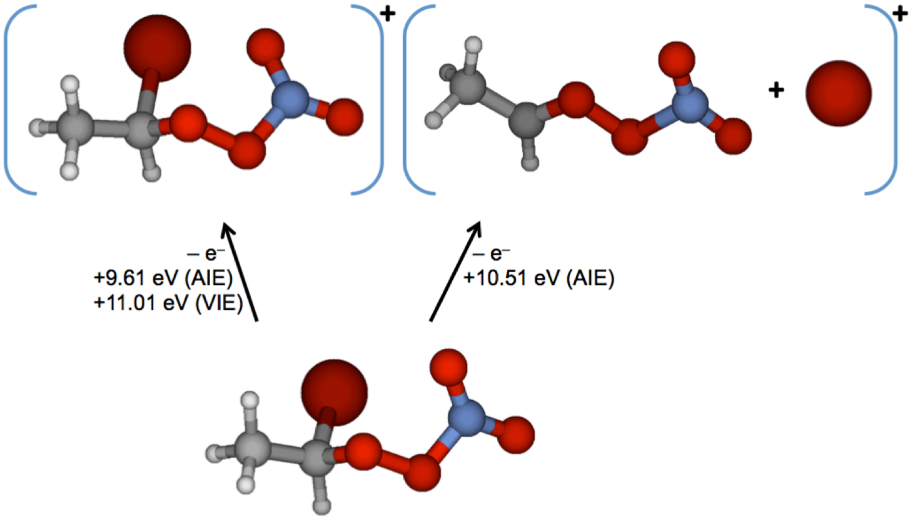
Use a chemical 'scrubber' for Criegees and examine the change in the signal

D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
D. Stone, M. Blitz, L. Daubney, N. U. Howes and P. Seakins, *Physical Chemistry Chemical Physics*, 2014, 16, 1139-1149.

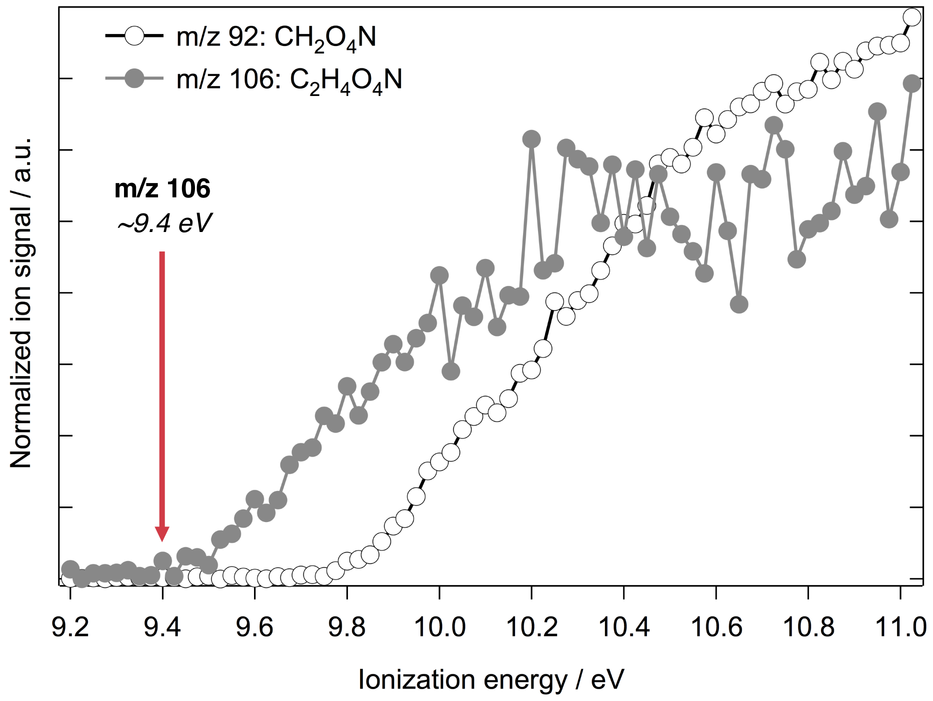
Ruling Out Side Chemistry in Adduct Formation: Ionization energy calculations

IE of **m/z 106 DI is 10.51 eV → Far above 9.4 eV experimental observation**

~<0.2 eV error in the calculated ionization energies from ωB97XD/ADZP.



Unlikely that dissociative ionization of $R_1CR_2IOONO_2$ leads to the observed signal at the Criegee-NO₂ adduct mass.



$RCR'IOO + NO_2 \longrightarrow RCR'IOONO_2 \xrightarrow{VUV,\ DI} \left[RCR'OONO_2\right]^+ + I$ Calculate onset energy of the DI

$RCR'IOO + NO_2 \longrightarrow RCR'OONO_2 + I$ Use a chemical ‘scrubber’ for Criegees and examine the change in the signal

How we calculate [Criegee]

- The diiodoalkane Criegee precursor is delivered to the reactor via a bubbler backed by He through an MFC.
- From the vapor pressure of the precursor, the temperature and pressure and flow rate of the bubbler, the concentration of the diiodoalkane can be obtained.
- The non-background subtracted data are utilized to obtain the % depletion of the precursor on photolysis.
- $[O_2]$>>[dioodoalkane], such that formation of Criegee intermediates from diodoalkyl + O_2 is fast.
- The Criegee concentration is obtained using the concentration of the depleted precursor multiplied by the estimated yield of Criegee at a given pressure from dioodoalkyl + O_2. The pressure dependent yields of Criegee Intermediates for the formaldehyde oxide measured by Stone *et al.* were utilized.

D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.

Ruling Out Side Chemistry in Adduct Formation

- **How do we know that the m/z 106 & m/z 92 signals are indeed from Criegee + NO_2 and not side chemistry ?**

$$RCR'OO + NO_2 \longrightarrow RCR'OONOO$$

- Iodoalkylperoxy (RCR’IOO) occurs from the reaction of iodoalkyl (RCR’I) with O_2 and is in competition with Criegee formation.

$$RCR'I + O_2 \longrightarrow RCR'OO + I$$

$$RCR'IOO$$

- The yield of formaldehyde oxide from iodoalkyl + O_2 was investigated by Stone *et al.* At 4 Torr (N_2) 64-99 % is achieved, and at 40 Torr (N_2), 64-86 %.
- At **higher pressures the reactions of iodoalkylperoxy radicals will be more pertinent** as their yields are enhanced.
- Estimated rate coefficient for iodoalkylperoxy radicals with NO_2 by Stone *et al.* is on the order of the Criegee + NO_2 rate coefficient measured in this and previous work.

Kinetics alone cannot rule out their contribution to m/z 106 and m/z 92.

$$RCR'IOO + NO_2 \longrightarrow RCR'IOONO_2 \xrightarrow{VUV,\ DI} \left[RCR'OONO_2\right]^{+} + I$$

Calculate onset energy of the DI

$$RCR'IOO + NO_2 \longrightarrow RCR'OONO_2 + I$$

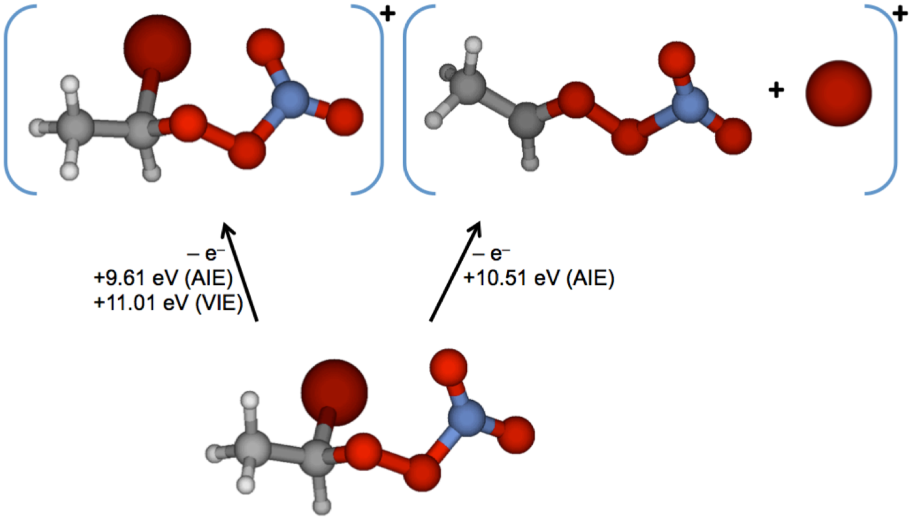
Use a chemical ‘scrubber’ for Criegees and examine the change in the signal

D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
D. Stone, M. Blitz, L. Daubney, N. U. Howes and P. Seakins, *Physical Chemistry Chemical Physics*, 2014, 16, 1139-1149.

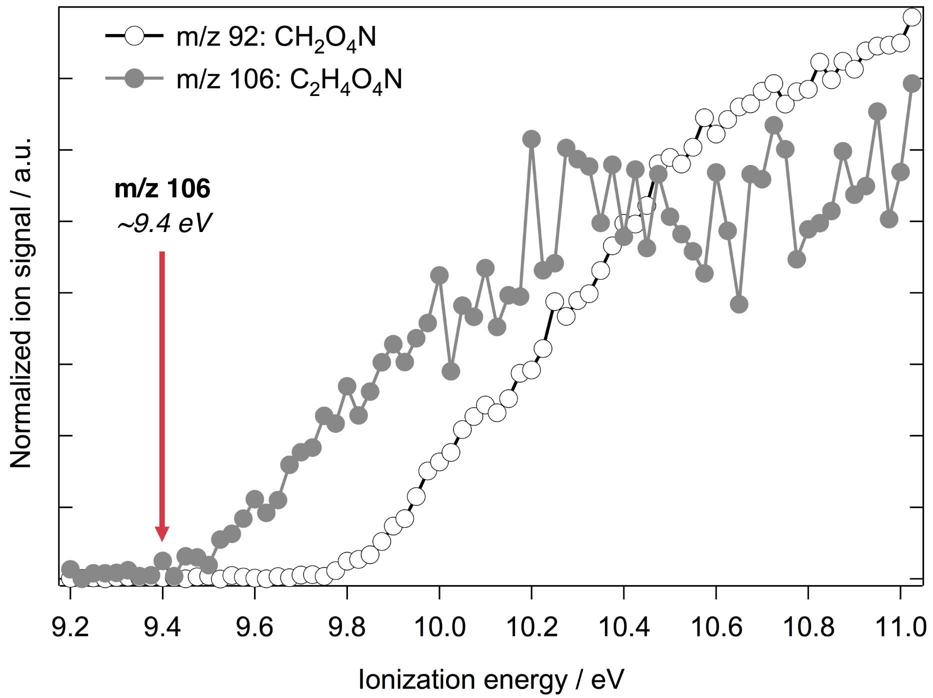
Ruling Out Side Chemistry in Adduct Formation: Ionization energy calculations

IE of **m/z 106 DI is 10.51 eV → Far above 9.4 eV experimental observation**

~<0.2 eV error in the calculated ionization energies from ωB97XD/ADZP.



Unlikely that dissociative ionization of $R_1CR_2IOONO_2$ leads to the observed signal at the Criegee-NO_2 adduct mass.



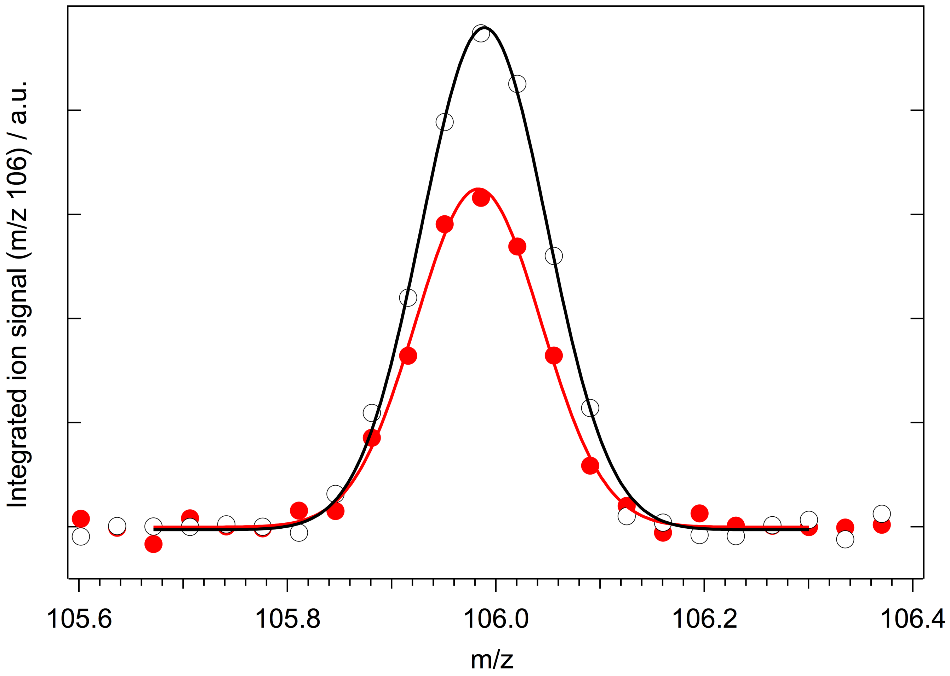
$RCR'IOO + NO_2 \longrightarrow RCR'IOONO_2 \xrightarrow{VUV,\ DI} \left[RCR'OONO_2\right]^+ + I$

Calculate onset energy of the DI

$RCR'IOO + NO_2 \longrightarrow RCR'OONO_2 + I$

Use a chemical ‘scrubber’ for Criegees and examine the change in the signal

Ruling Out Side Chemistry in Adduct Formation: Addition of SO_2



Signal depleted by ~ 30 %: Suggests that the adduct is indeed substantially if not entirely from Criegee + NO_2 reaction.

Acetaldehyde oxide + NO_2 measurements also performed in the presence of SO_2.

SO_2 + Criegee is very fast (*syn*-C2 2.9×10^{-11} molecule^{-1} cm^3 s^{-1}) so would act as a **scrubber for Criegees, removing them before they can react with NO_2.**

CH_2IOO + SO_2 recently found to be rapid by Huang *et al.* (~1-2 × 10^{-12} molecule-^{1} cm^3 s^{-1}), but a **factor of 10 slower than CH_2OO + SO_2.**

Addition of SO_2 will remove both R_1CR_2OO and R_1CR_2IOO, but at sufficiently **different rates** that **adduct origin can be determined by the amount of depletion in adduct signal.**

Removal of CH_3CHIOO by SO_2 and NO_2 anticipated to be equal, whereas removal of Criegee by SO_2 will be more effective by a factor of 10 (for *syn* - which we predominantly sample) or 100 (for *anti*).

Rate of *syn*-C2 + NO_2 is 7% of *syn*-C2 + SO_2: [SO_2] at 7 % [NO_2] used: 50 % of Criegee removal from each reaction.

If the adduct formation is due to **side chemistry SO_2 will have a negligible effect on the signal amplitude (~ %7).**

Adduct signal should be removed by ~ 50 % if due to Criegee + NO_2.

~~$RCR'IOO + NO_2 \longrightarrow RCR'IOONO_2 \xrightarrow{VUV,\ DI} \left[RCR'OONO_2\right]^+ + I$~~

Calculate onset energy of the DI

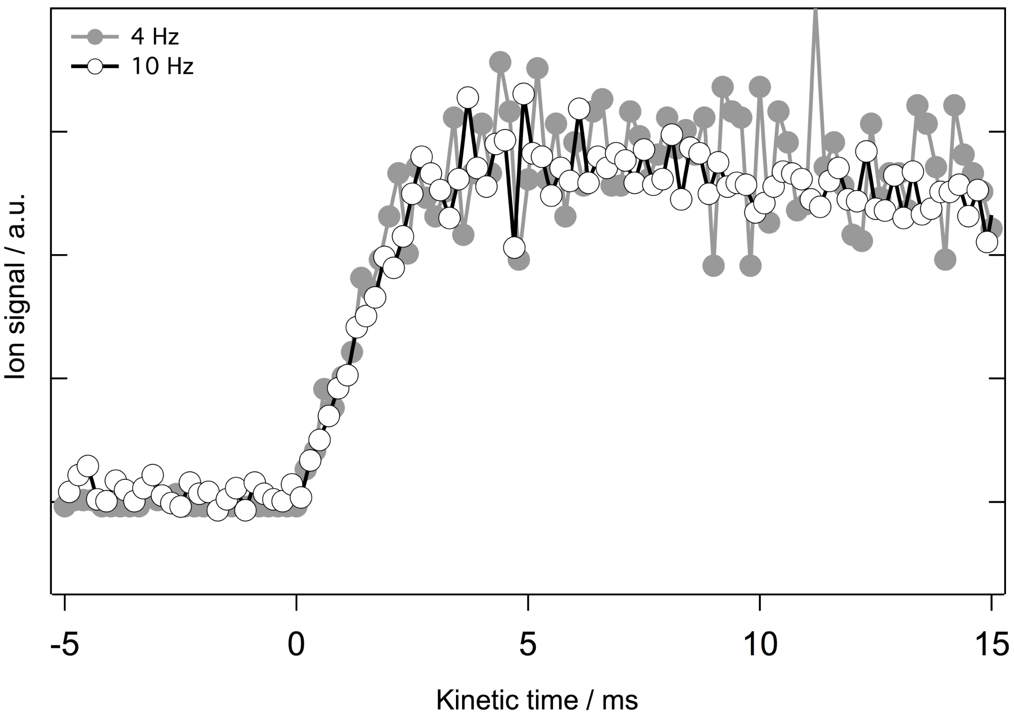
$RCR'IOO + NO_2 \longrightarrow RCR'OONO_2 + I$

Use a chemical ‘scrubber’ for Criegees and examine the change in the signal

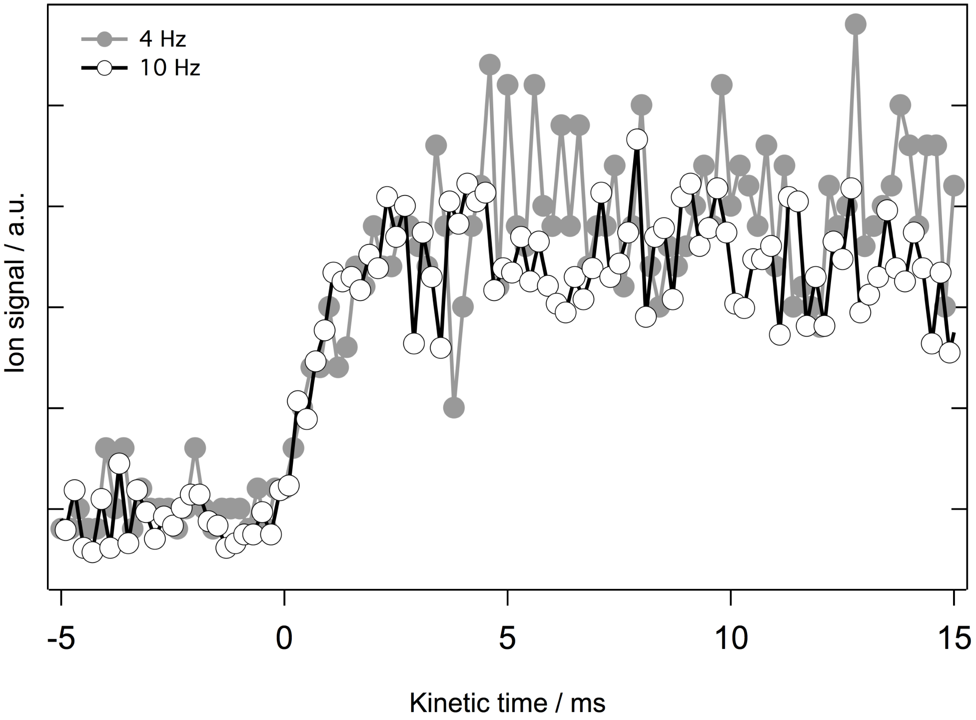
C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.
M. Huang, N. Kline, T. A. Miller and R. Dawes, *The Journal of Physical Chemistry A*, 2017, 121, 98-112.
D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.

4 Hz vs. 10 Hz

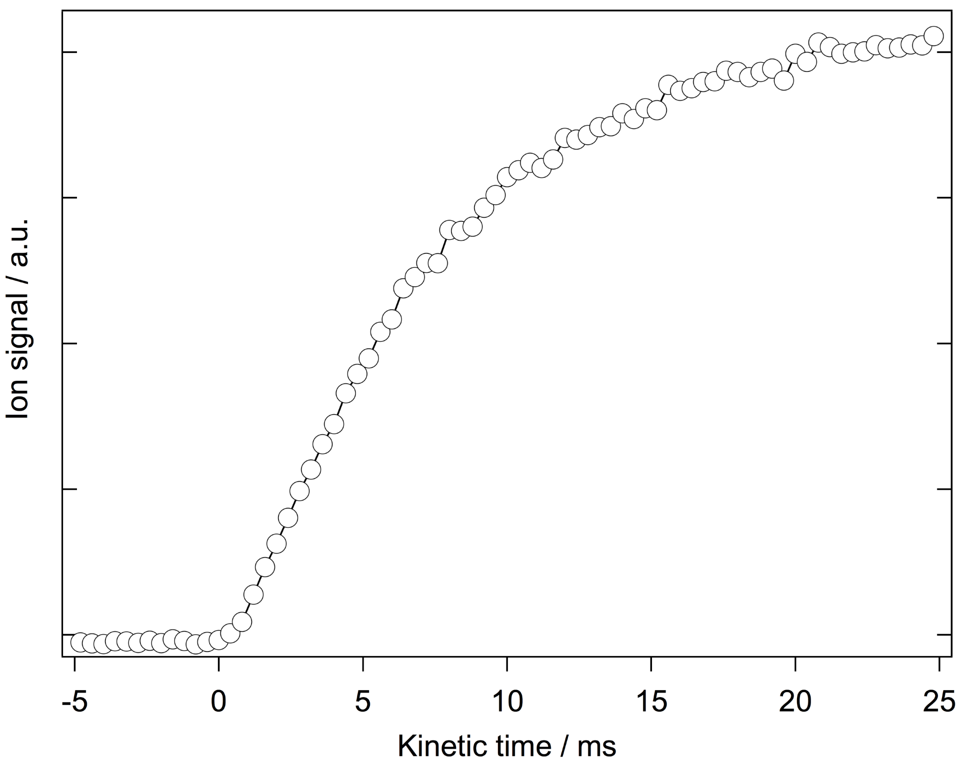
m/z 92 : Formaldehyde oxide + NO_2, 30 Torr, 300 K
$NO_2 = 3.9 \times 10^{14}$ molecule cm^3



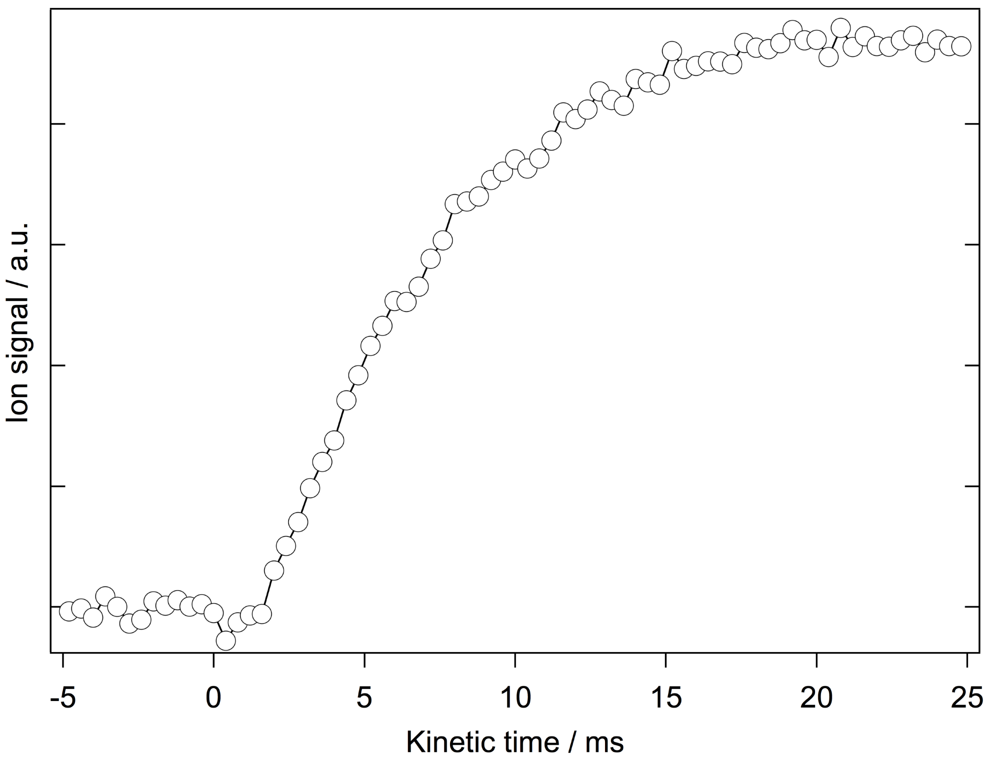
m/z 106 : Acetaldehyde oxide + NO_2, 40 Torr, 300 K
$NO_2 = 6.9 \times 10^{14}$ molecule cm^3



I_2 signal (IE = 9.3074 eV)



m/z 254 : Formaldehyde oxide + NO_2, 40 Torr, 300 K, 9.2-9.45 eV
$NO_2 = 5.2 \times 10^{14}$ molecule cm^3



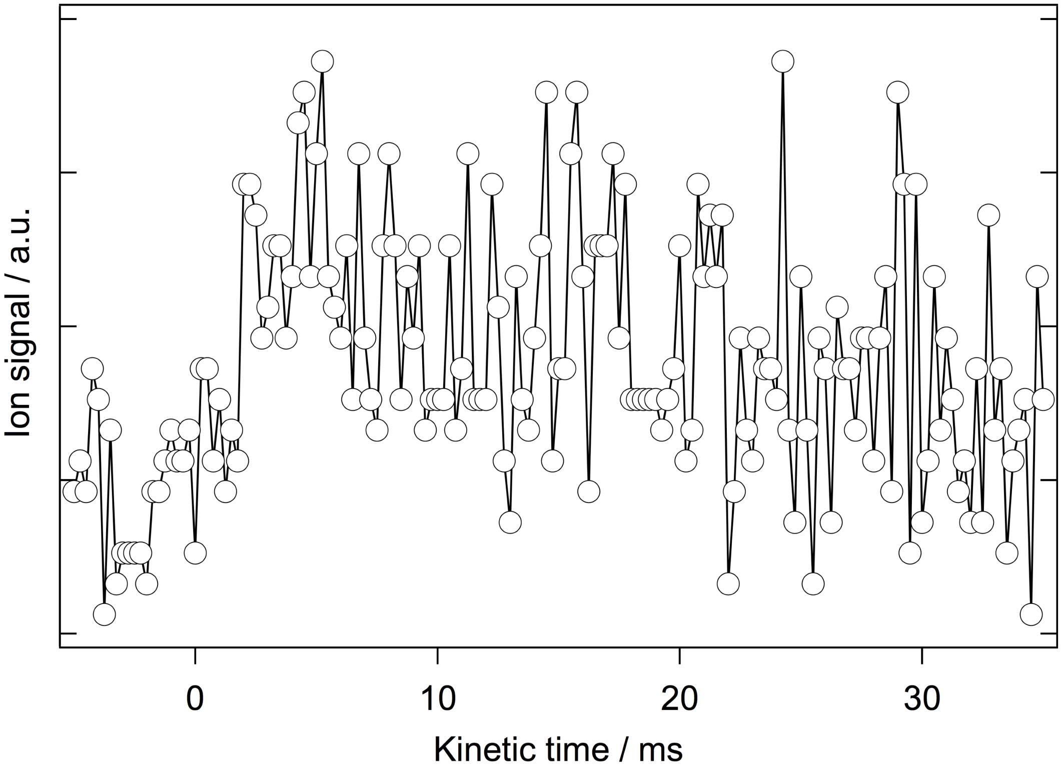
m/z 254 : Acetaldehyde oxide + NO_2, 40 Torr, 300 K, 9.2-9.45 eV
$NO_2 = 5.2 \times 10^{14}$ molecule cm^3

Non-instantaneous signal consistent with relatively slow recombination of I atoms rather than photolytic production.

M. Cockett, R. Donovan and K. Lawley, *The Journal of Chemical Physics*, 1996, 105, 3347-3360
S. Lias, in *Ionization Energy Evaluation in NIST Chemistry WebBook, NIST Standard Reference Database Number 69* eds. P. Linstrom and W. Mallard, National Institute of Standards and Technology, Gaithersburg MD..

m/z 189 signal: $IONO_2$?

m/z 189 : Formaldehyde oxide + NO_2, 30 Torr, 300 K, 11.5 eV
$NO_2 = 3.9 \times 10^{14}$ molecule cm^{-3}



$IONO_2$ (m/z 189) can be made either from IO + NO_2, or I_2 + NO_3.

I_2 + NO_3 second order rate coefficient is **1.5×10^{-12} molecule^{-1} cm^3 s^{-1}** but this is **limited by the formation of I_2 from I atom recombination**.

IO + NO_2 effective second order rate coefficient **~ 3×10^{-13} molecule^{-1} cm^3 s^{-1}** at 30 Torr of He, 300 K. **[NO_2] = 3.9×10^{14}**.

I + I effective second order rate coefficient **~3×10^{-15} molecule^{-1} cm^3 s^{-1}** at 30 Torr of He, 300 K. From the % depletion of CH_2I_2, the maximum I atom concentration is going to be **~ 6×10^{13} molecule cm^{-3}. The maximum NO_3 concentration will be less than this.**

Given the bimolecular rate coefficient for the NO_2 reaction, and the NO_2 concentration are significantly greater than for I + I, **IO + NO_2 is more likely to be the contributing factor to the m/z 189 signal, if it is indeed $IONO_2$.**

No absolute PI spectrum of $IONO_2$: Cannot quantify it.

I_2 + NO_3: R. Chambers, A. Heard and R. Wayne, *The Journal of Physical Chemistry*, 1992, 96, 3321-3331.
I + I: D. Baulch, J. Duxbury, S. Grant and D. Montague, *J. Phys. Chem. Ref. Data*, 1981, 10.
IO + NO_2: F. Maguin, G. Laverdet, G. Le Bras and G. Poulet, *The Journal of Physical Chemistry*, 1992, 96, 1775-1780.
E. Daykin and P. Wine, Journal of Physical Chemistry, 1990, 94, 4528-4535.
S. P. Sander, R. Friedl, D. Golden, M. Kurylo, G. Moortgat, P. Wine, A. Ravishankara, C. Kolb, M. Molina and B. Finlayson-Pitts, Jet Propulsion Laboratory, California Institute of Technology Pasadena, California, Chemical kinetics and p