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

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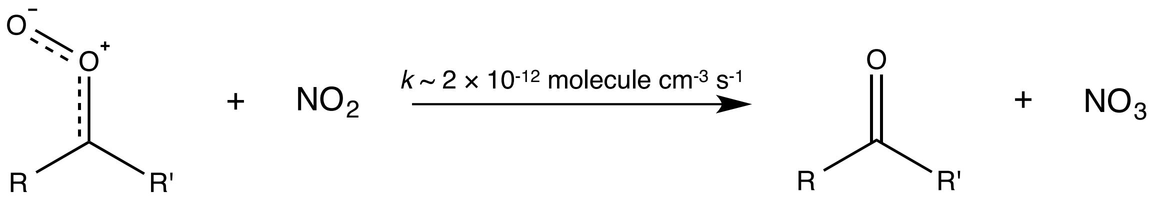
Atmospheric Chemistry in the Anthropocene : Faraday Discussion
Tuesday 23rd May 2017
Paper 13206

The Importance of Criegee + NO_2



- 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**.
  - Up to **~22% of *syn*-acetaldehyde oxide removal** in high NO_x mega-cities (Vereecken *et al.*)
  - Up to **~40 % of NO_3** yield from the principal pathway, $O_3 + NO_2$ **assuming 100 % yield of NO_3 from the reaction**

- Laboratory observations of products somewhat conflicting
  - ***Increase* in acetone signal with NO_2** consumption in an ozonolysis study of TME by Presto and Donahue.
  - ***Decrease* in formaldehyde/acetaldehyde/acetone signal with NO_2** observed in photolytically-generated direct Criegee intermediate studies (Stone *et al.*, Taatjes *et al.* & Chhantyal-Pun *et al.*).
  - Evidence for NO_3 observed in the form of **N_2O_5** (Ouyang *et al.*)

$$NO_3 + NO_2 \rightleftharpoons N_2O_5$$

  - Low NO_3 which **could be rationalized by side chemistry** (Lewis *et al.)*

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

To fully assess the impact of this reaction in the atmosphere, the products need to be understood.

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.,
D. Stone, M. Blitz, L. Daubney, N. U. Howes and P. Seakins, *Physical Chemistry Chemical Physics*, 2014, 16, 1139-1149.
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.
L. Vereecken, H. Harder and A. Novelli, *Physical Chemistry Chemical Physics*, 2012, 14, 14682-14695.
A. A. Presto and N. M. Donahue, *The Journal of Physical Chemistry A*, 2004, 108, 9096-9104.
T. R. Lewis, M. A. Blitz, D. E. Heard and P. W. Seakins, *Physical Chemistry Chemical Physics*, 2015, 17, 4859-4863.
B. Ouyang, M. W. McLeod, R. L. Jones and W. J. Bloss, *Physical Chemistry Chemical Physics*, 2013, 15, 17070-17075.

Products of Acetaldehyde Oxide + NO_2 : Acetaldehyde + NO_3

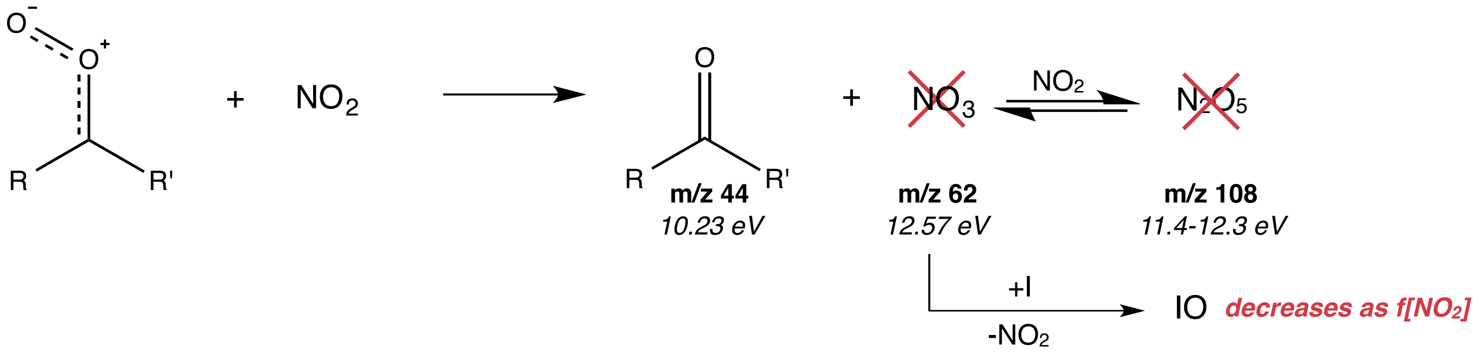
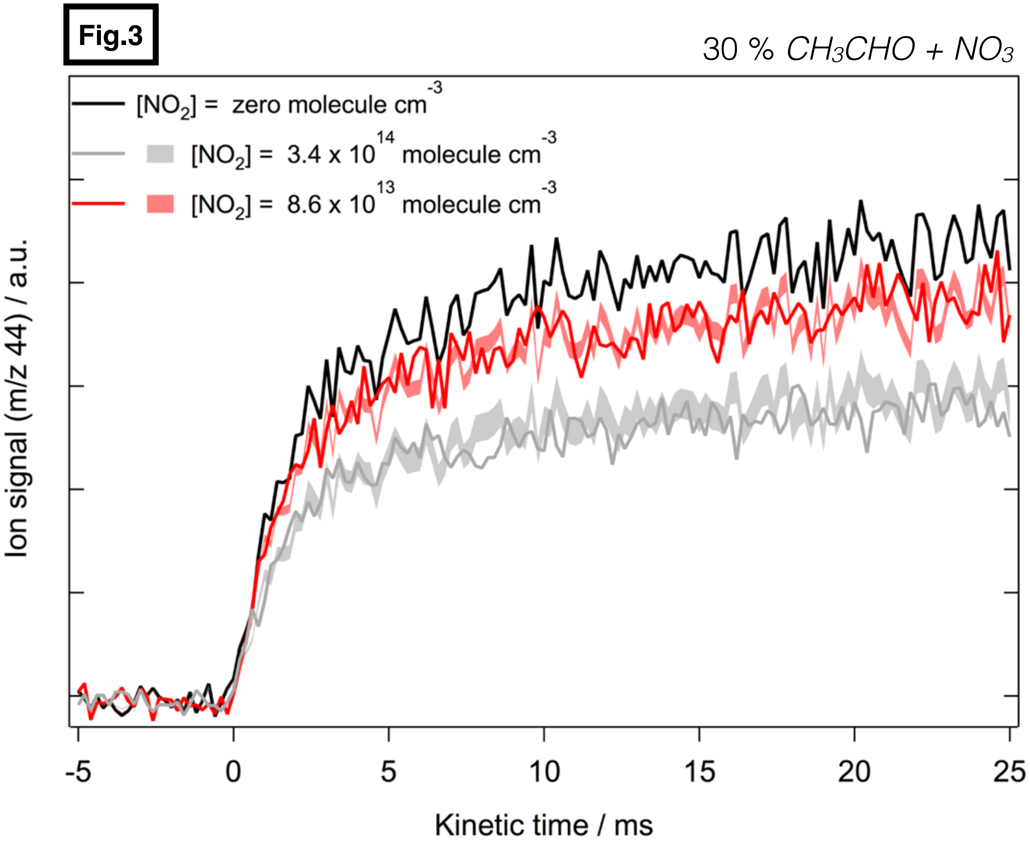


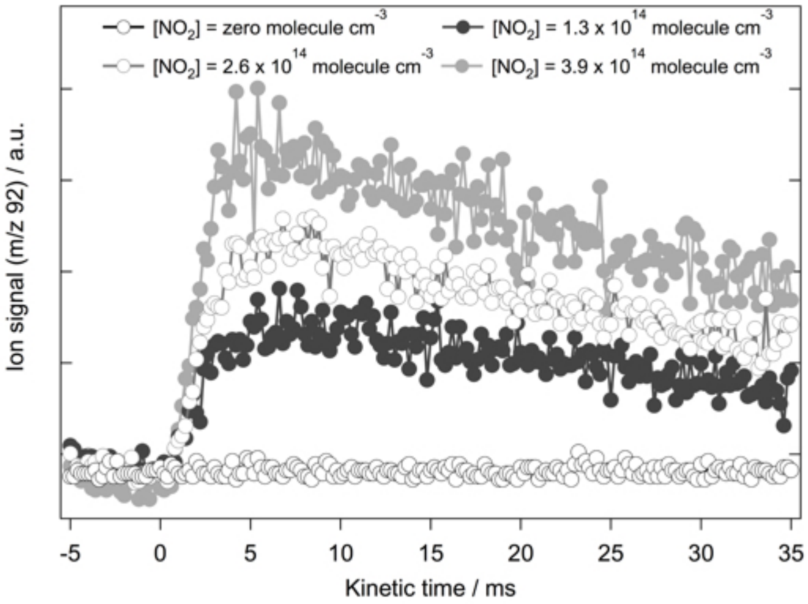
Fig.3



- **Do not observe NO_3** despite stable cation.
- **Do not observe N_2O_5**.
- **IO signal *decreases* as function of [NO_2]**, however IO is also produced from Criegee + I, so this is **inconclusive**.
- **Acetaldehyde signal *decreases* with increasing NO_2**
- Model of signal as *f*[NO_2] gives an **upper limit of ~30 % for NO_3 + acetaldehyde.**

P. Monks, L. Stief, M. Krauss, S. Kuo, Z. Zhang and R. Klemm, *The Journal of Physical Chemistry*, 1994, 98, 10017-10022.
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.
R. Chambers, A. Heard and R. Wayne, *The Journal of Physical Chemistry*, 1992, 96, 3321-3331.
T. J. Gravestock, M. A. Blitz, W. J. Bloss and D. E. Heard, *ChemPhysChem*, 2010, 11, 3928-3941.

Products of Acetaldehyde Oxide + NO_2 : Adduct



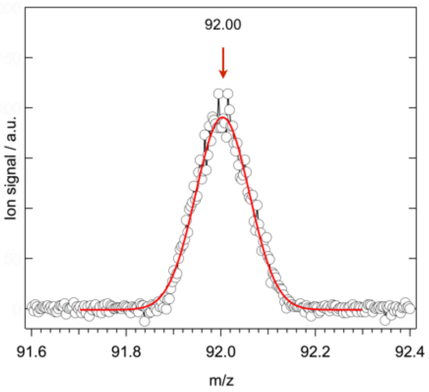
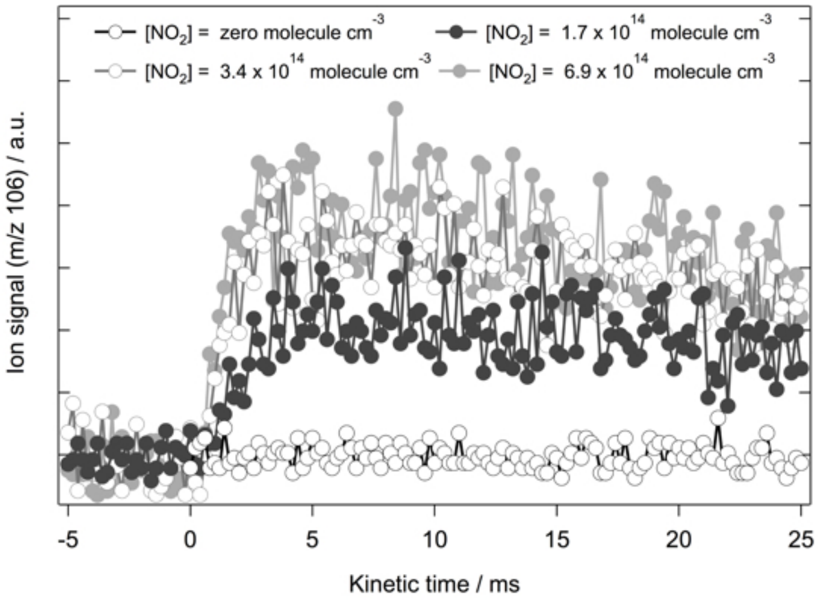


Fig.6 *Formaldehyde oxide + NO_2*
30 Torr, 300 K, 10.5 eV

- **Signal observed at m/z consistent with Criegee-NO_2 adduct** chemical formulae (**CH_2O_4N** and **$C_2H_4O_4N$** respectively)
- Signals are **[NO_2]- and time-dependent signals**
- Experimental photoionization spectra allows comparison with calculated structures



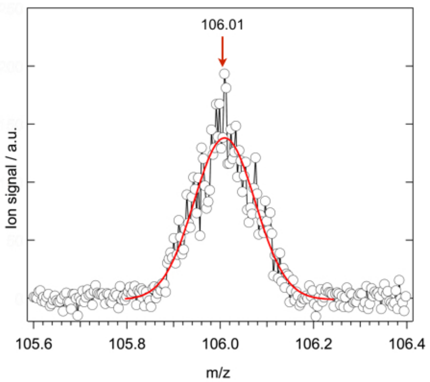


Fig.7 *Acetaldehyde oxide + NO_2*
40 Torr, 300 K, 10.5 eV

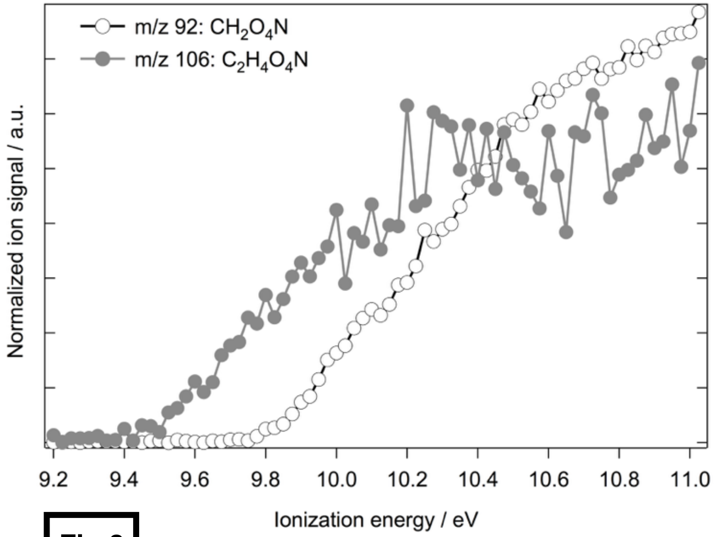
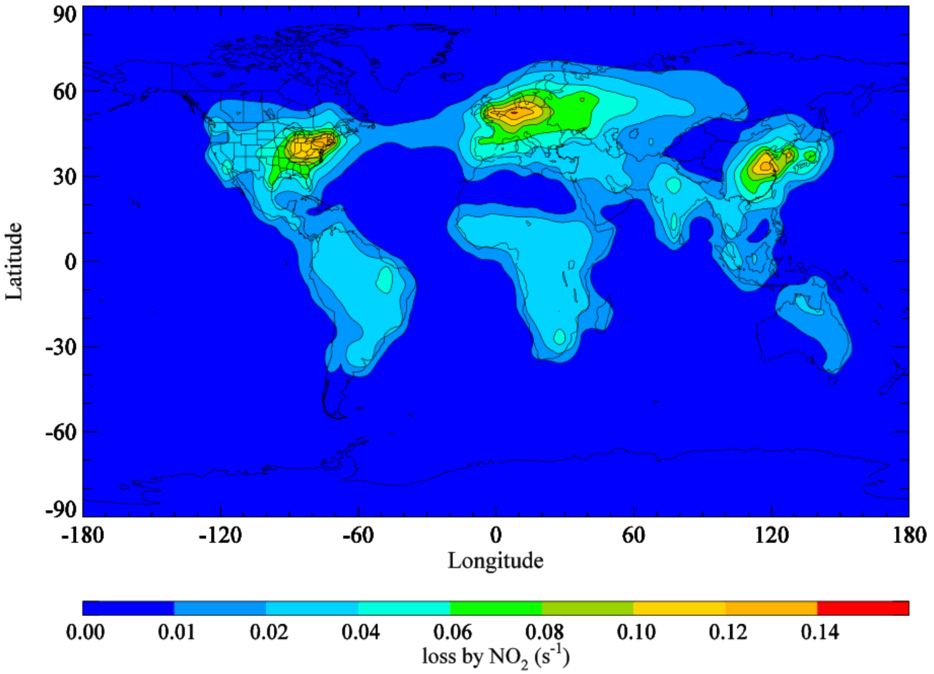


Fig.8

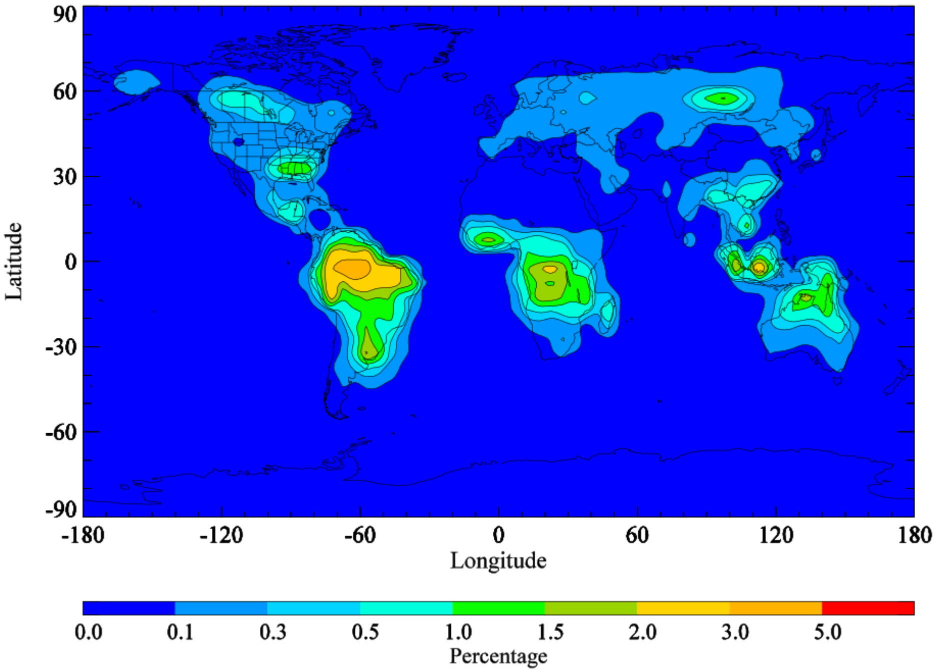
C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke and D. K. W. Mok, *Science*, 2013, 340, 177-180.

Atmospheric impact

Fig.12



- **Impact of Criegee + NO_2 on Criegee intermediate global loss found to be minimal, <0.15 s^{-1}**
- Impact largest around large cities in the northern hemisphere**.**
- Unimolecular loss represents a much greater loss still.



- **Negligible impact on NO_3 production compared to the principal production pathway (O_3 + NO_2).**
- Increase is **found to be < 4 % with a 100 % yield of NO_3.**
- Accounting for the revised upper limit of ~ 30 %, this effect will be lessened.

To assess the true impact of this reaction on NO_3, the atmospheric fate and impact of the adduct needs to be understood

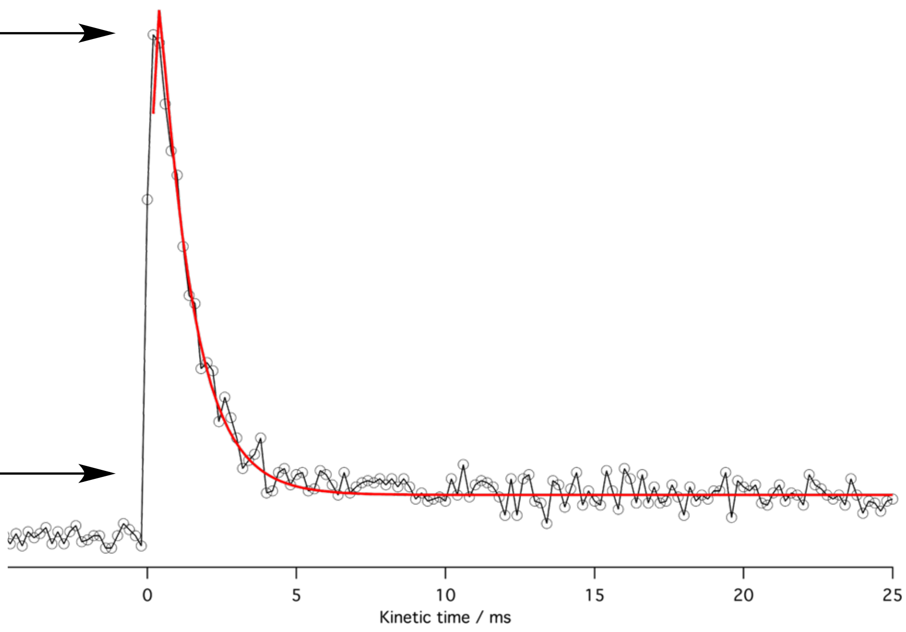
S. R. Utembe, M. C. Cooke, A. T. Archibald, M. E. Jenkin, R. G. Derwent and D. E. Shallcross, *Atmospheric Environment*, 2010, 44, 1609-1622., S. R. Utembe, M. C. Cooke, A. T. Archibald, D. E. Shallcross, R. G. Derwent and M. E. Jenkin, *Atmospheric environment*, 2011, 45, 1604-1614., S. R. Utembe, L. 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.

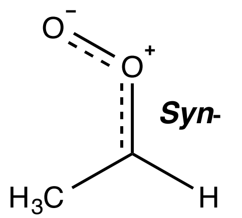
Y-axis offset on Criegee Kinetic Trace due to Isomerization

Fig. 5

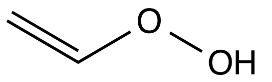
Maximum

Foot

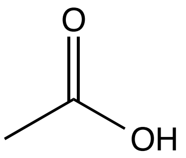




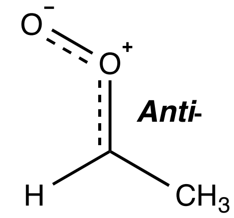
Syn-



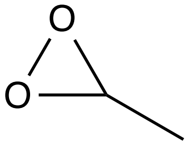
Vinylhydroperoxide
9.18 eV



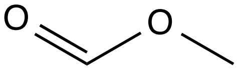
Acetic acid
10.7eV



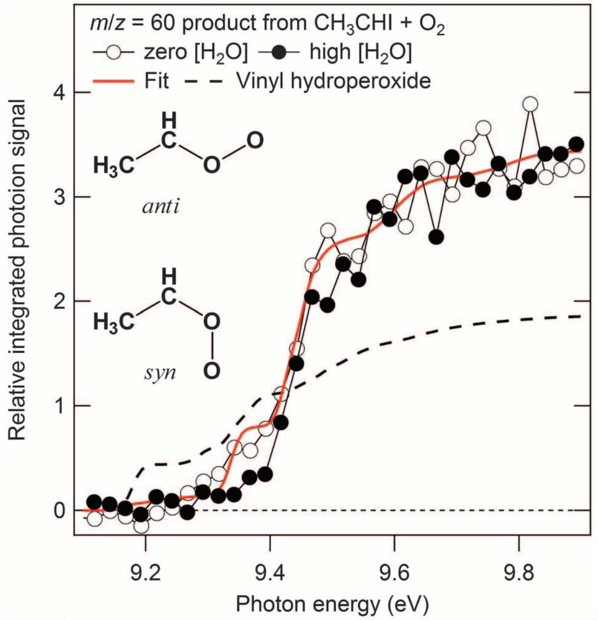
Anti-

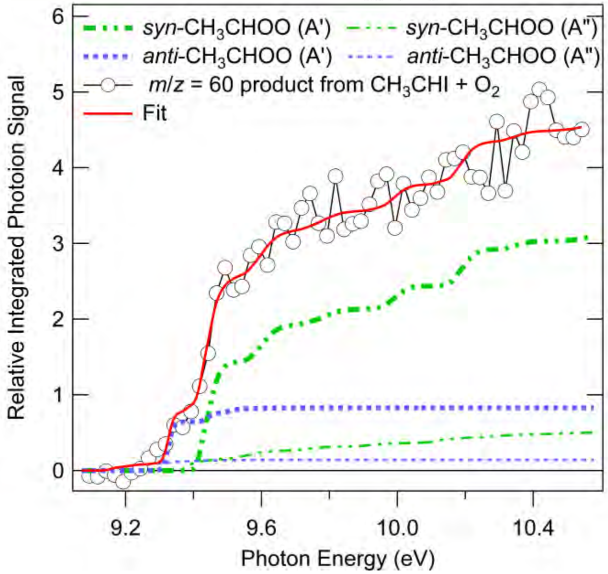


Methyldioxirane
10.36 eV



Methyl formate
10.8 eV





Reproduced from Taatjes et al., Science, 2013.

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.

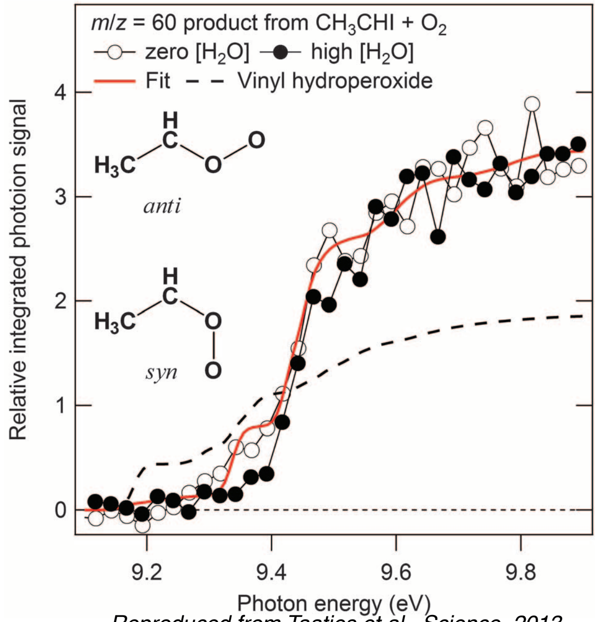
No evidence of NO_2-facilitated isomerization

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



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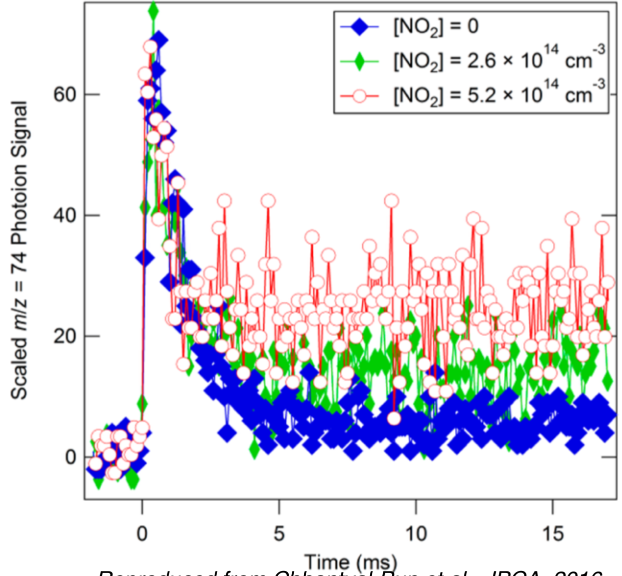
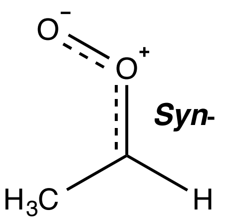
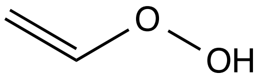


Reproduced from Chhantyal-Pun et al., JPCA, 2016



Syn-



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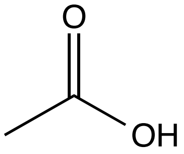

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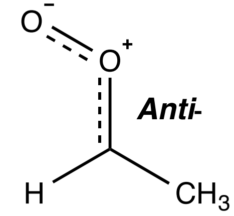
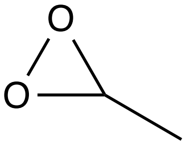


Anti-



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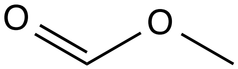

Methyl formate

10.8 eV

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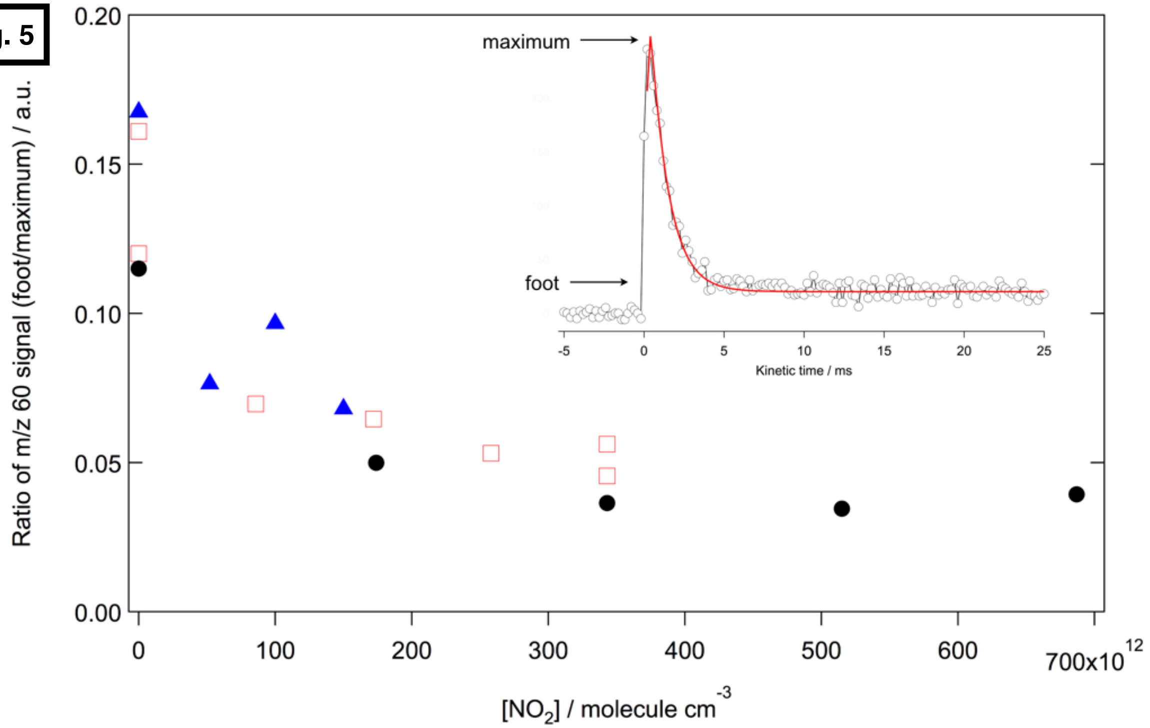
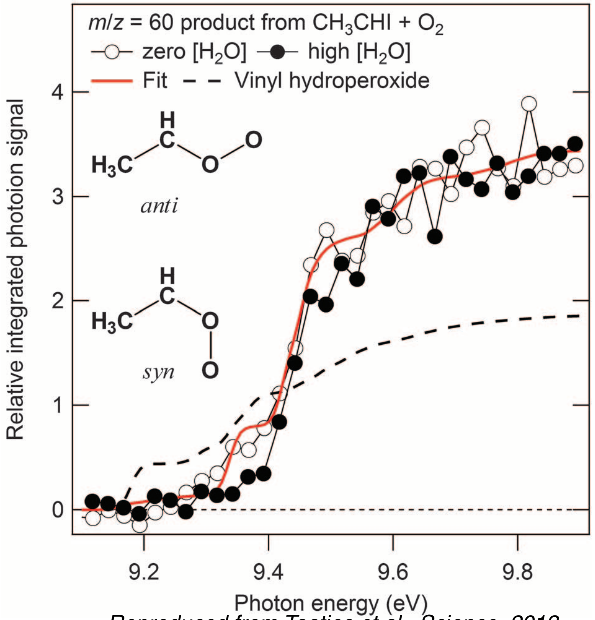
No evidence of NO_2-facilitated isomerization

Fig. 5





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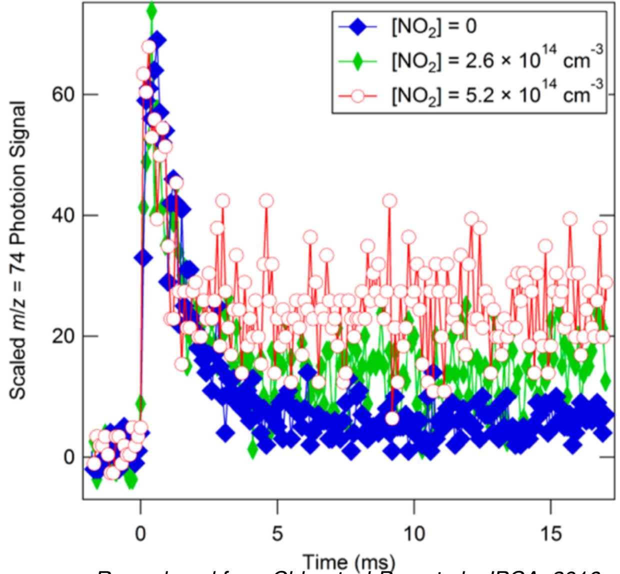

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At 10.5 eV, we observe contributions to m/z 60 from *anti*- and *syn*-acetaldehyde oxide as well as **vinyl hydroperoxide and methyl dioxirane.**

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.

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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 $[NO_2]$.

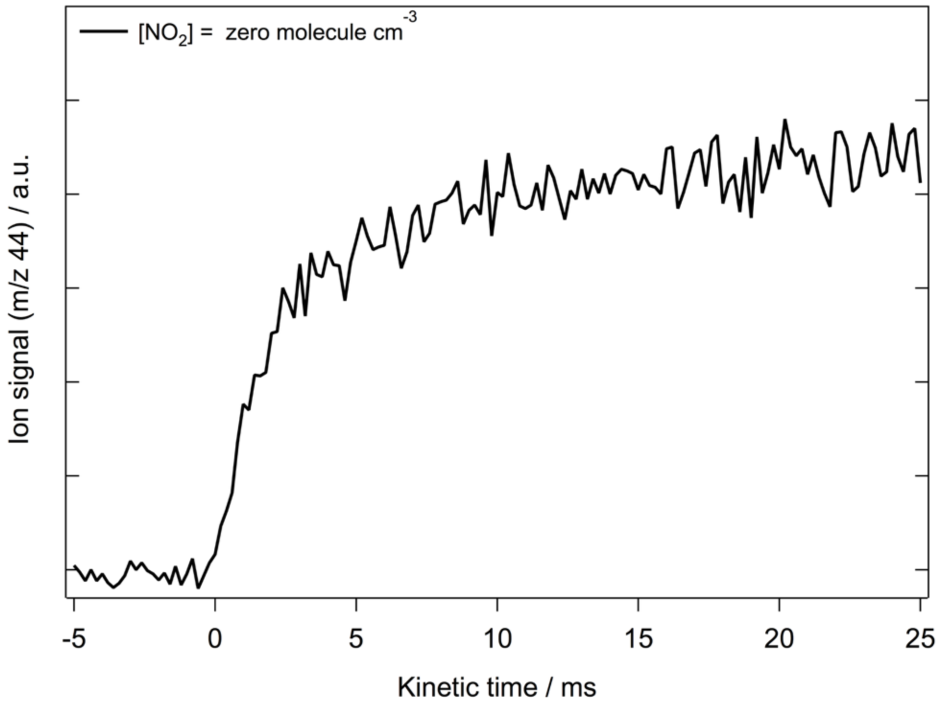
% CI Loss due to reaction = $(k'_{NO2}/(k'_{NO2}+k'_{intercept})) \times 100$.

The anticipated signal can be calculated by the following:

$Signal_{(NO2)} = Signal_{(no\ NO2)} \times (100\% - (\%\ CI\ loss\ due\ to\ reaction \times 1\text{-}Yield))$

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.



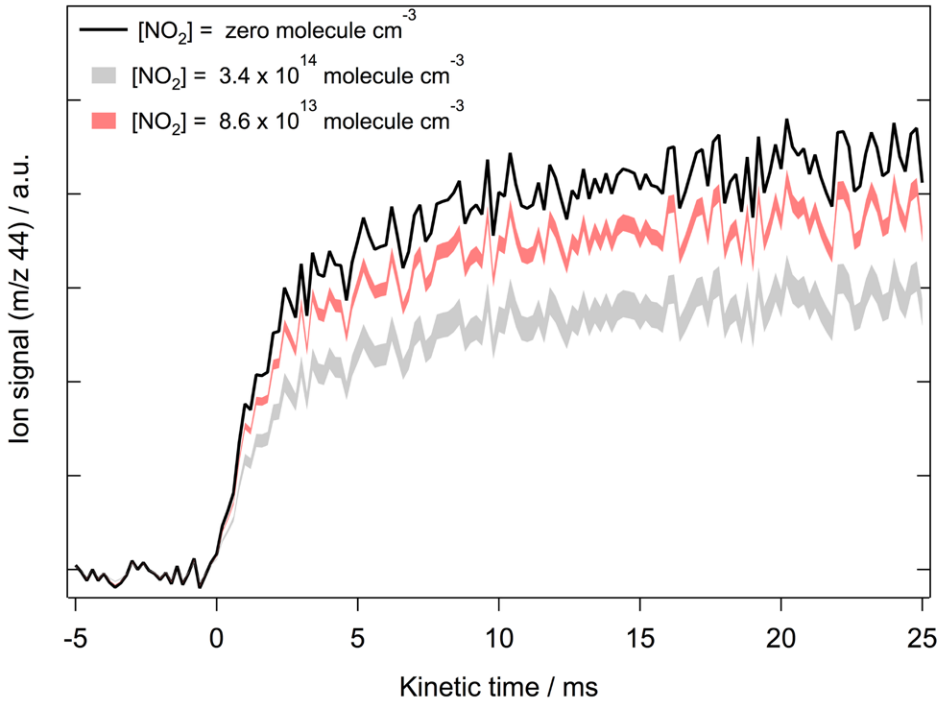


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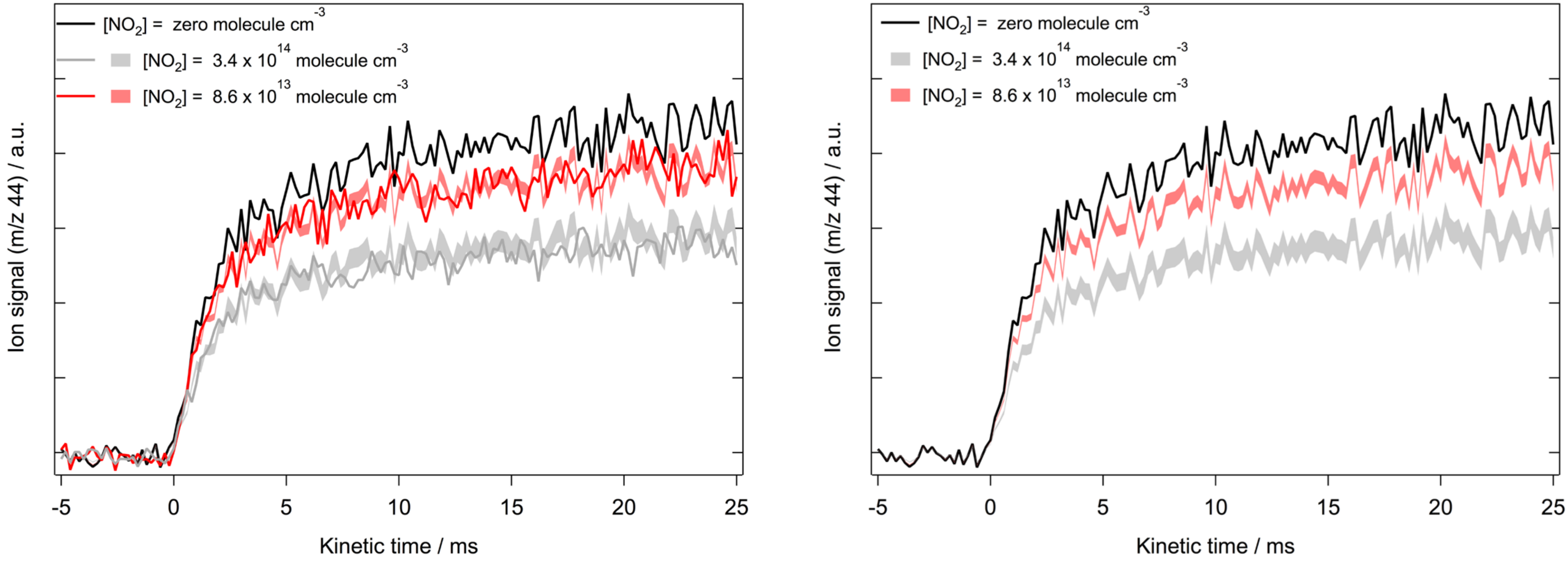
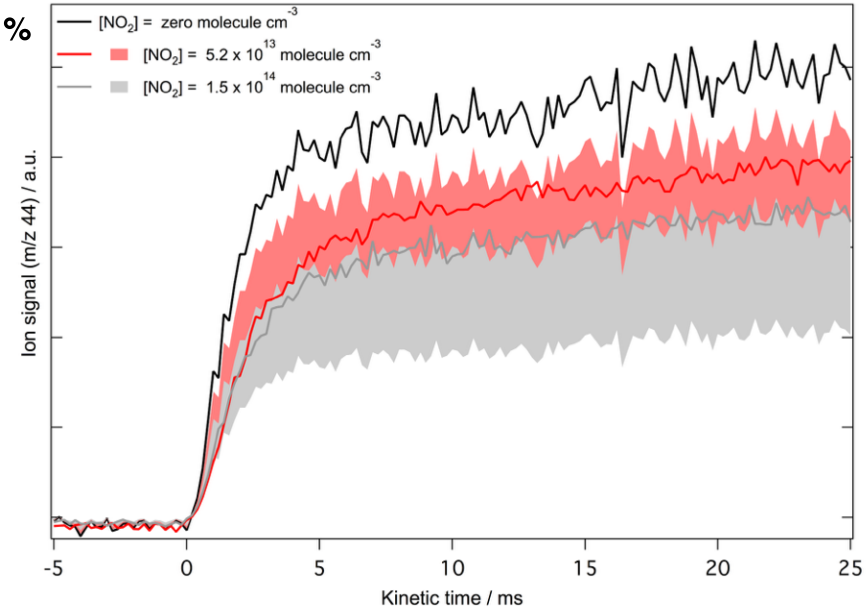
Fig.3



30 % CH_3CHO + NO_3

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

0 %



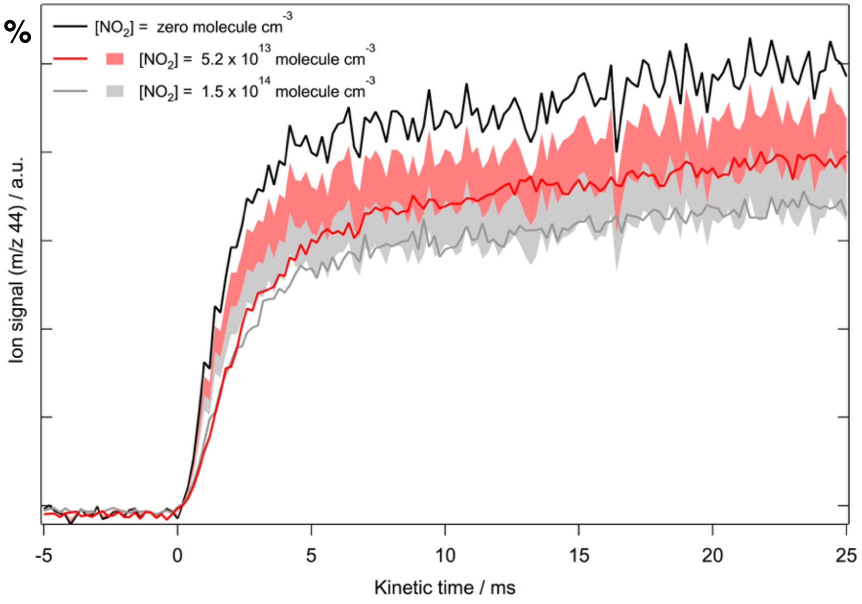
If the branching ratio of Criegee + NO_2 is pressure dependent, the bimolecular channel will have the highest yield at lower pressures.

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**.

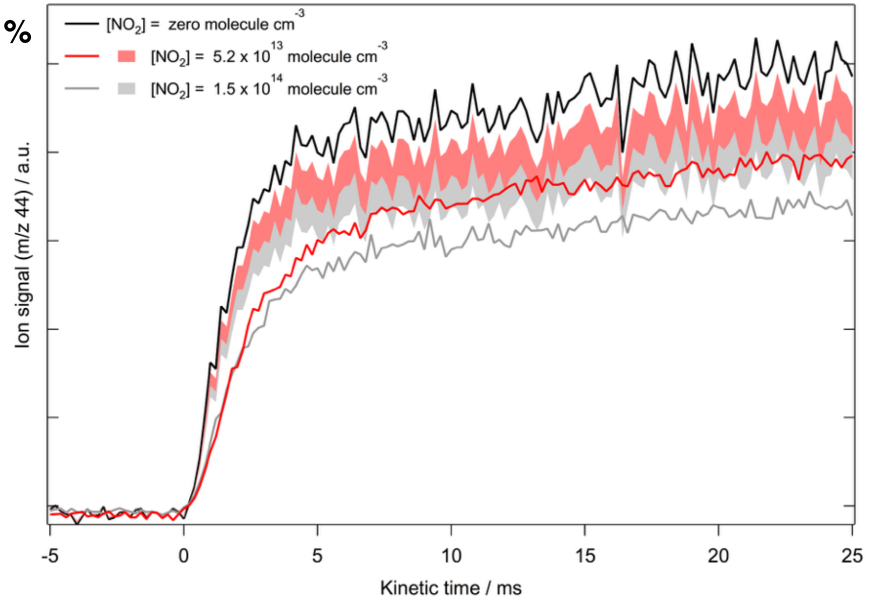
However, the **error on our bimolecular rate coefficient is larger** and so the error bands on the corresponding predicted acetaldehyde signals in the presence of NO_2 are larger.

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

30 %



50 %

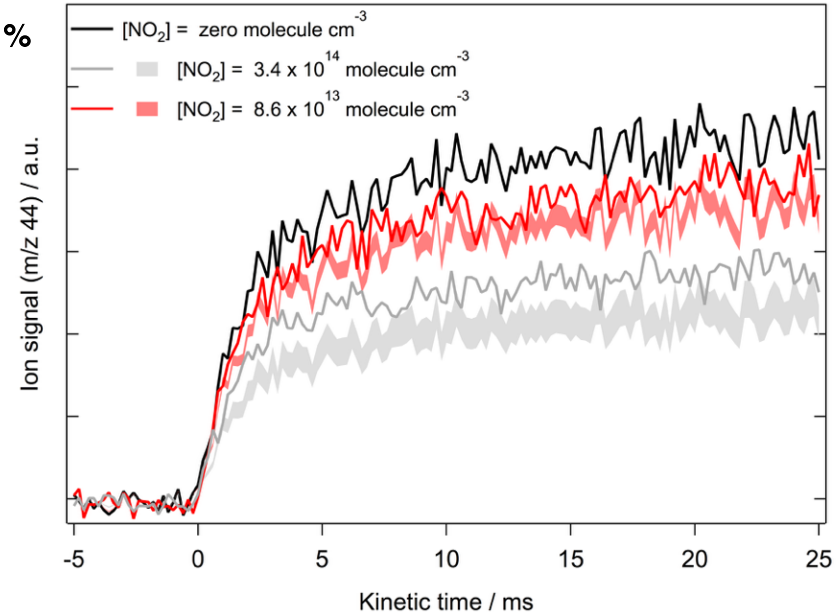


D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.
T. J. Gravestock, M. A. Blitz, W. J. Bloss and D. E. Heard, *ChemPhysChem*, 2010, 11, 3928-3941.

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

Fig. 3

0 %

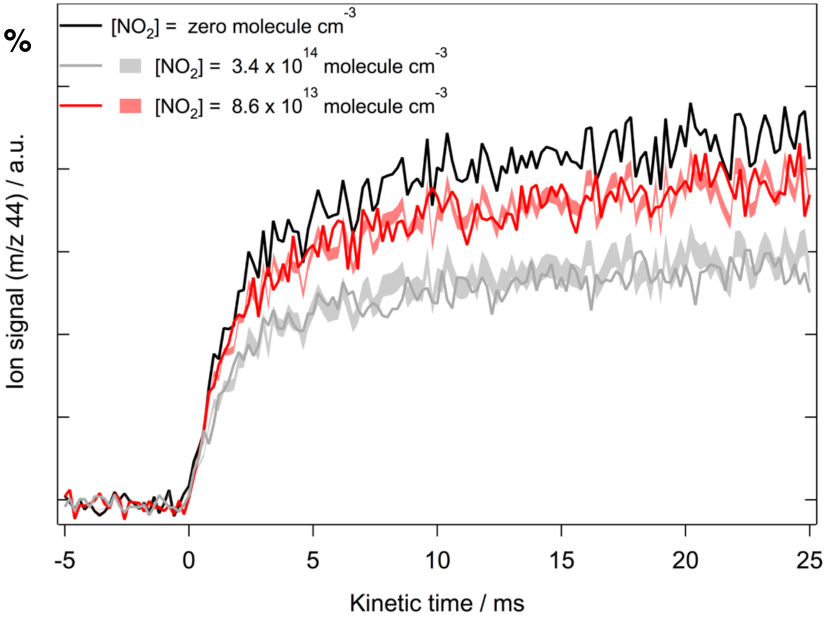


If the branching ratio of Criegee + NO_2 is pressure dependent, the bimolecular channel will have the highest yield at lower pressures.

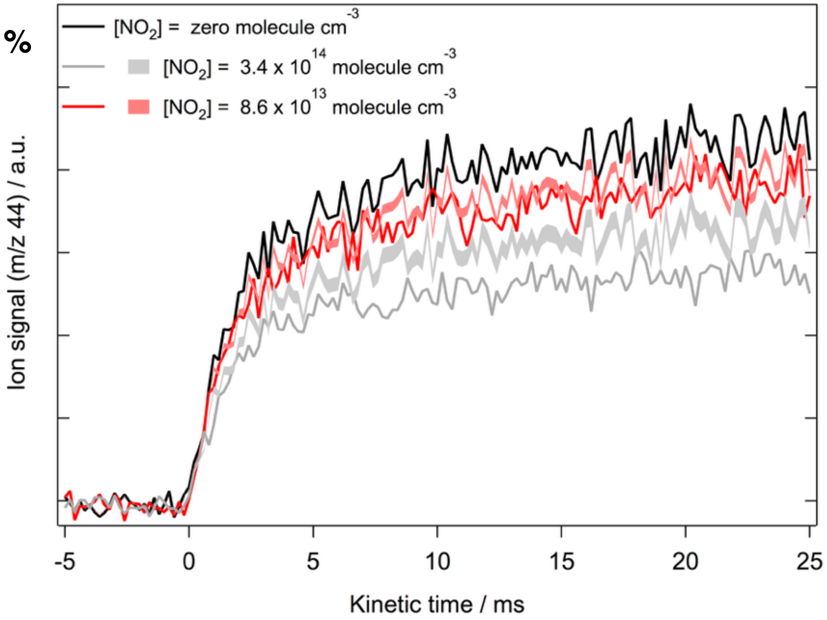
The **yield of Criegee from RCR’I + O_2 is slightly lower at 20 Torr (67-93 % for C1 at 20 Torr N_2) at lower pressures**: Side chemistry from **RCR’IOO + I → RCR’O + IO + I is more relevant, we do not attempt to account for this.**

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

30 %



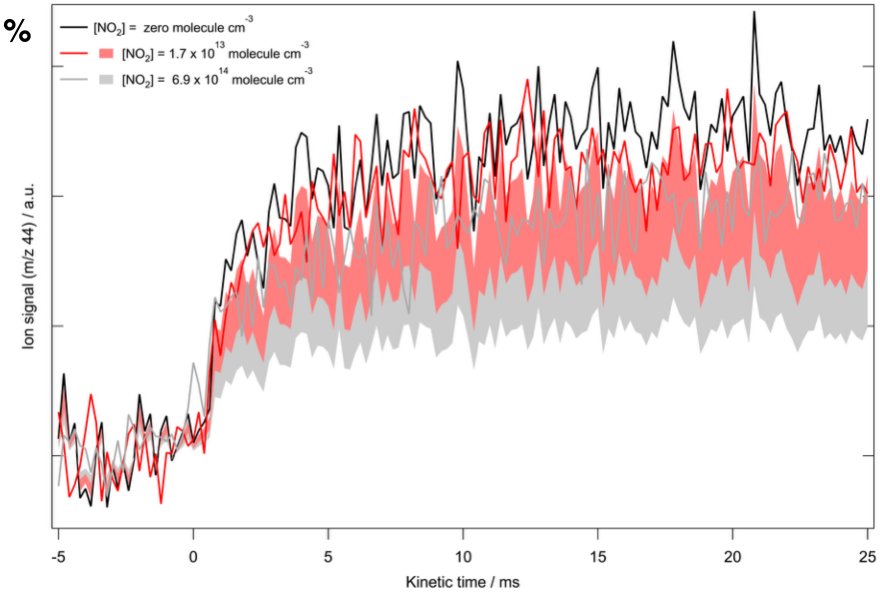
50 %



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 %

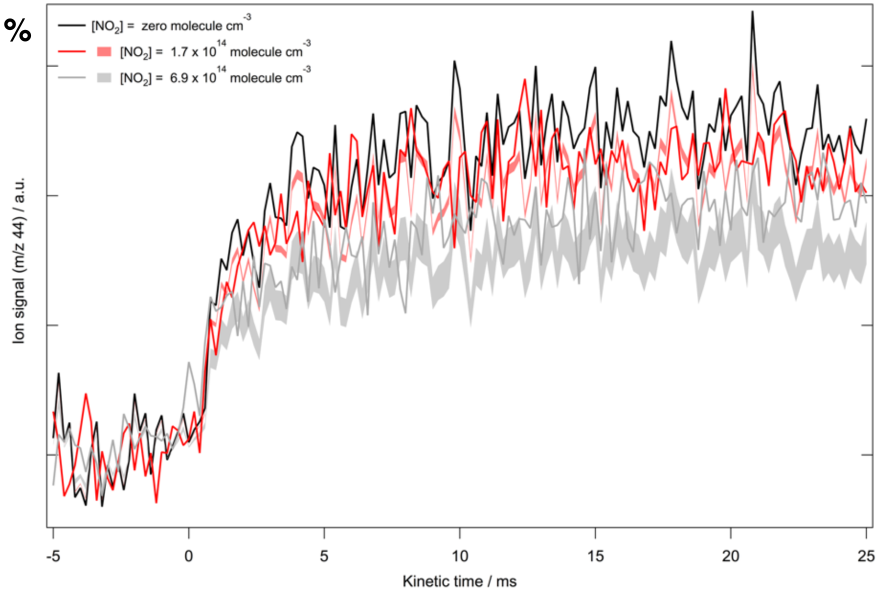


If the branching ratio of Criegee + NO_2 is pressure dependent, the bimolecular channel will have the highest yield at lower pressures.

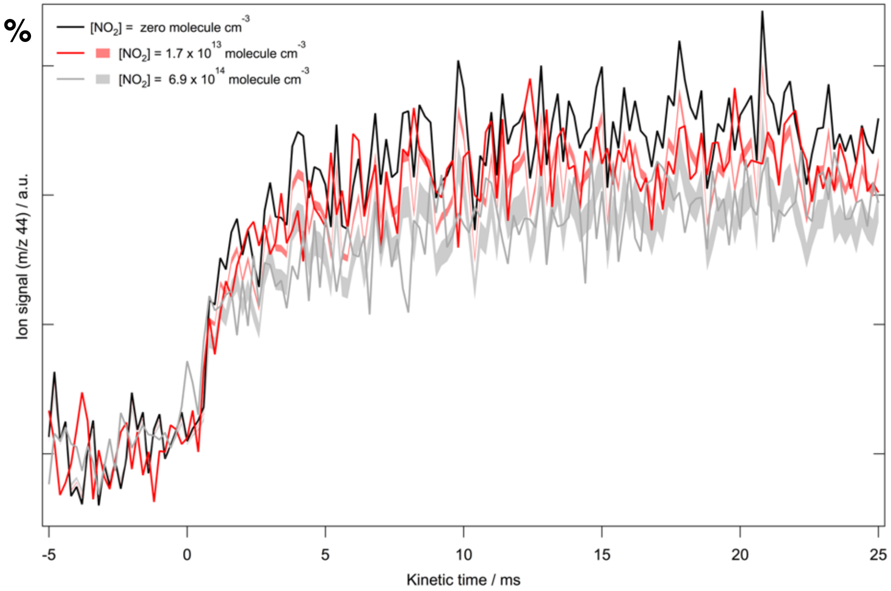
The **yield of Criegee from RCR'I + O_2 is slightly lower at 20 Torr (64-86 % for C1 at 40 Torr N_2) at lower pressures**: Side chemistry from **RCR'IOO + I → RCR'O + IO + I is more relevant, we do not attempt to account for this.**

~**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

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

1. Reactions of Criegee

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

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

2. Reactions of iodoalkylperoxy

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

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

$$\mathrm{CH_3CHIO} \longrightarrow \mathrm{CH_3CHO + I} \qquad \text{Fast ! (for C1)}$$

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 ~ 3.5 × 10^{-11} molecule^{-1} cm^{3} s^{-1} (for C1)*

$CH_3CHIOO + CH_3CHIOO \longrightarrow 2CH_3CHIO + O_2$ *k ~ 9 × 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 ~ 1-2 × 10^{-12} molecule^{-1} cm^{3} s^{-1} (estimated, based on Huang et al.)*

[NO$_2$] ~ 10^{14} molecule^{-1} cm^{3} & [I] ~ 10^{13} molecule^{-1} cm^{3}
Reactions of CH$_3$CHIOO 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.

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

- 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.

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

Calculate onset energy of the DI

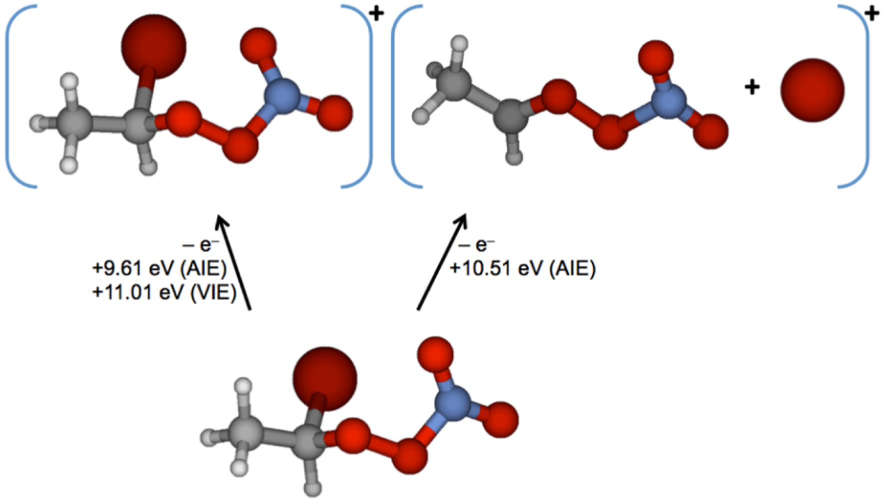
$$\mathrm{RCR'IOO + NO_2 \longrightarrow RCR'OONO_2 + I}$$

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

Fig.10

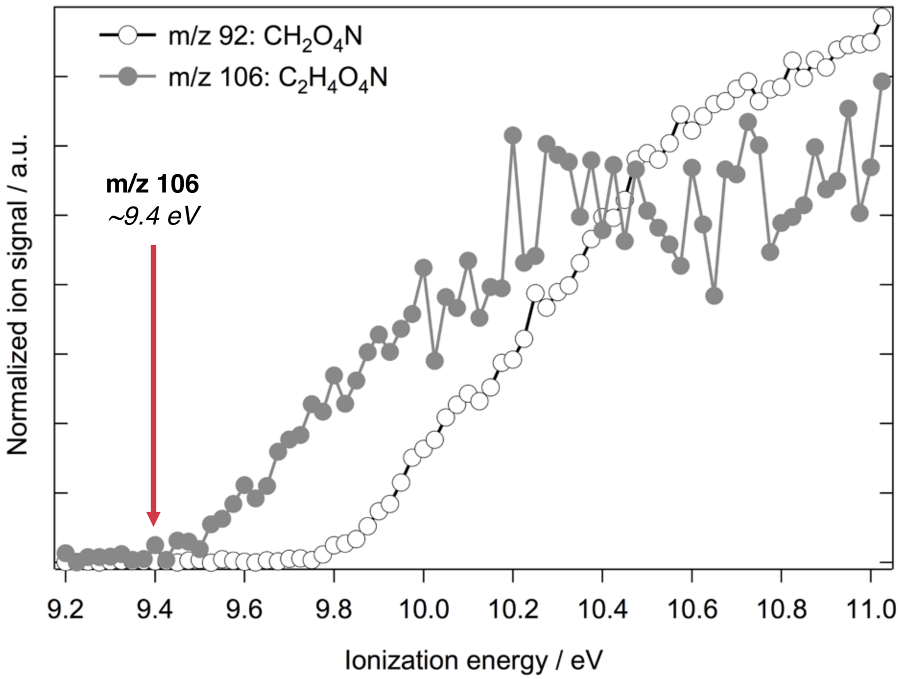


Unlikely that dissociative ionization of $R_1CR_2IOONO_2$ leads to the observed signal at the Criegee-NO_2 adduct mass.

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.

Fig.8

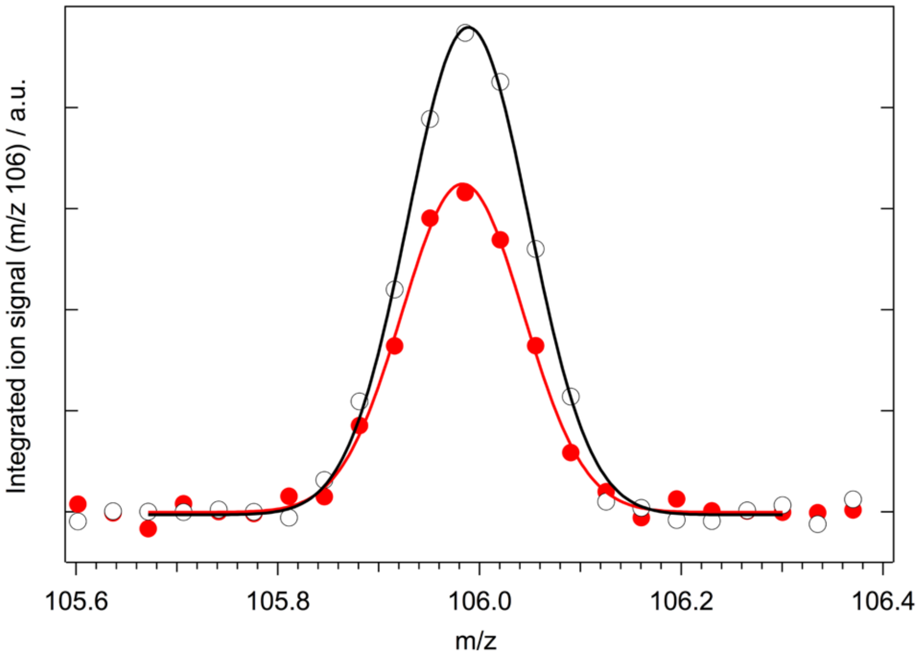


$RCR'IOO + NO_2 \longrightarrow RCR'IOONO_2 \xrightarrow{VUV,\ DI} \left[RCR'OONO_2\right]^+ + I$ Calculate onset energy of the DI

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

Ruling Out Side Chemistry in Adduct Formation: Addition of SO_2

Fig.11



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.

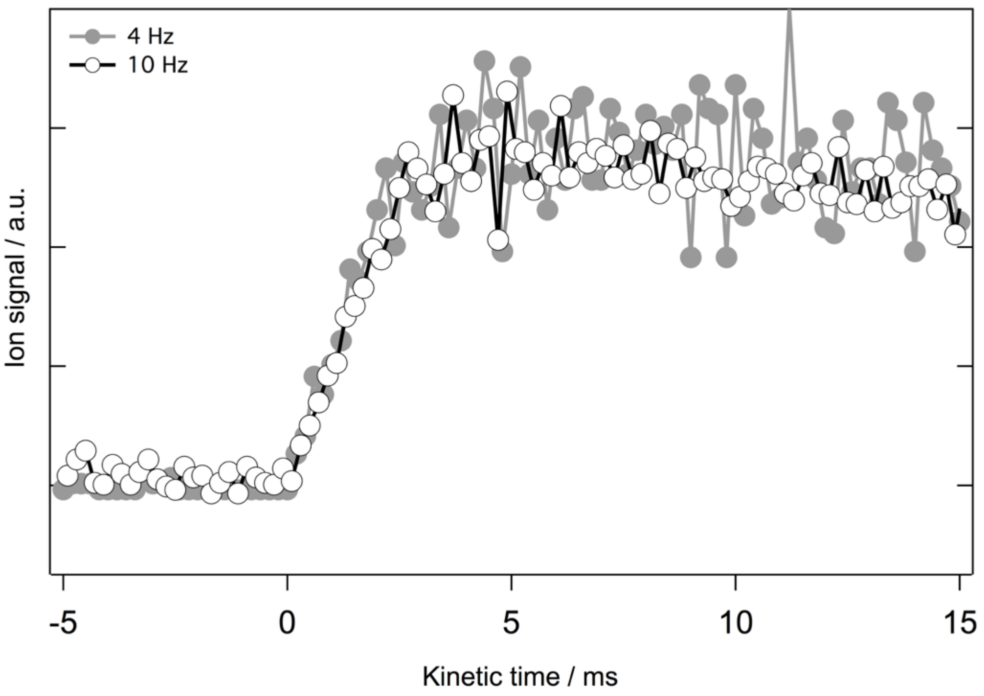
How we calculate [Criegee]

- 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.

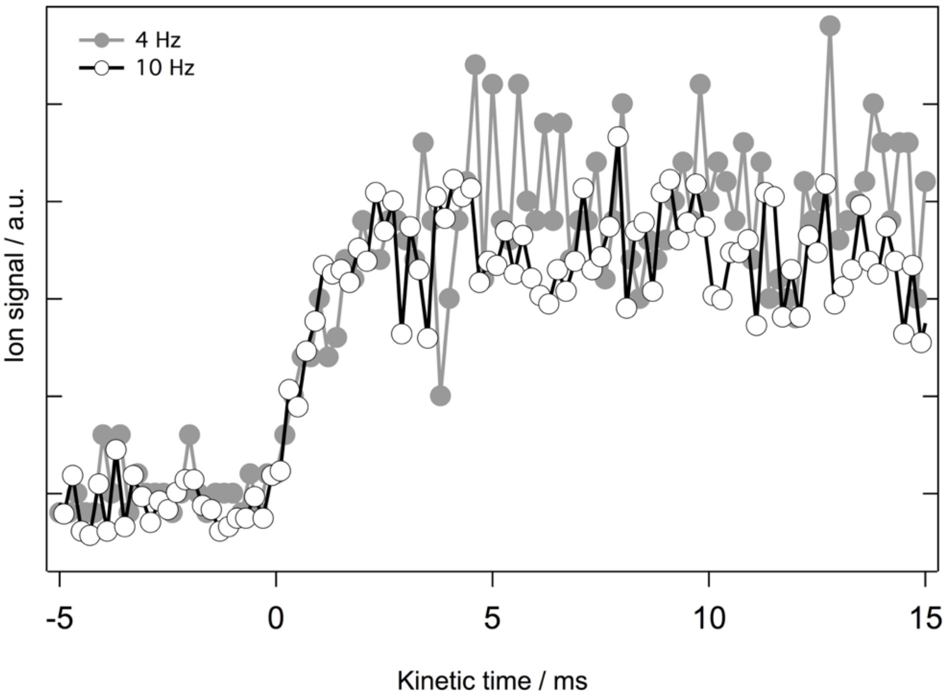
D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *Physical Chemistry Chemical Physics*, 2013, 15, 19119-19124.

4 Hz vs. 10 Hz

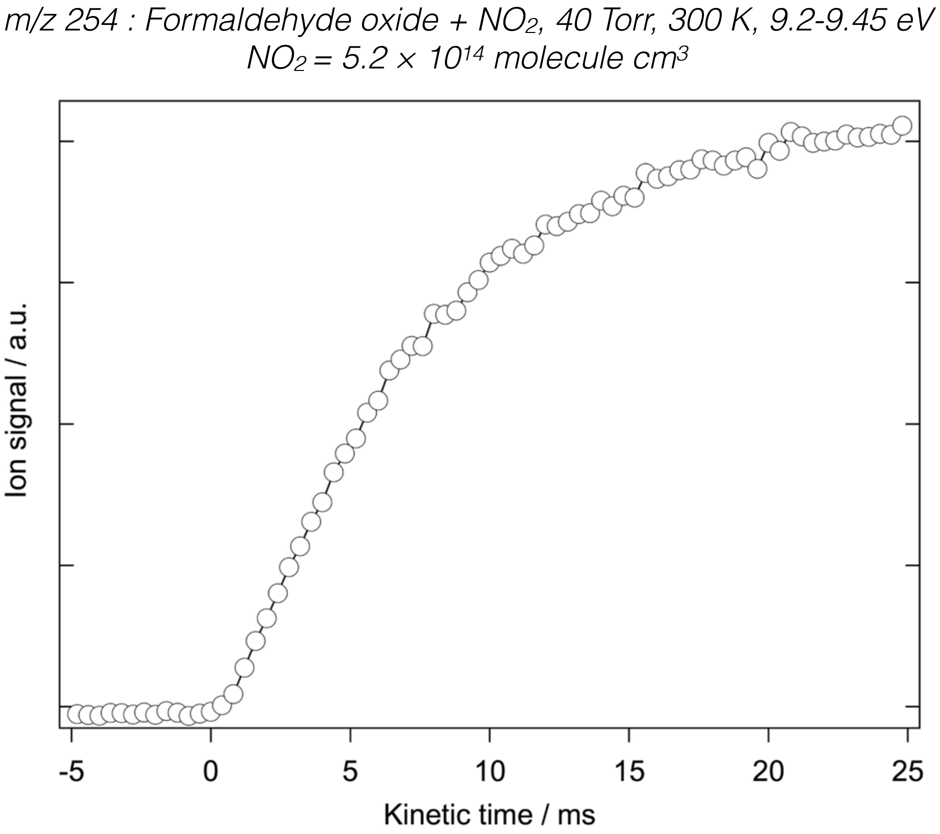
m/z 92 : Formaldehyde oxide + NO_2, 30 Torr, 300 K
$NO_2 = 3.9 \times 10^{14}$ molecule cm^3

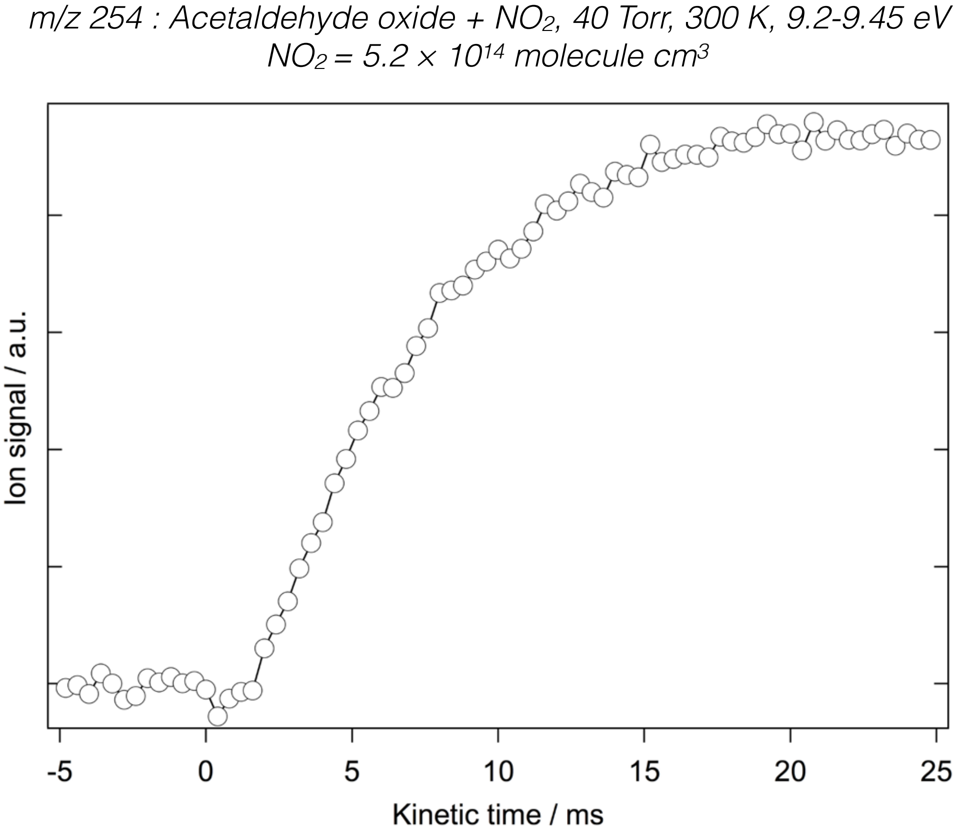


m/z 106 : Acetaldehyde oxide + NO_2, 40 Torr, 300 K
$NO_2 = 6.9 \times 10^{14}$ molecule cm^3



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

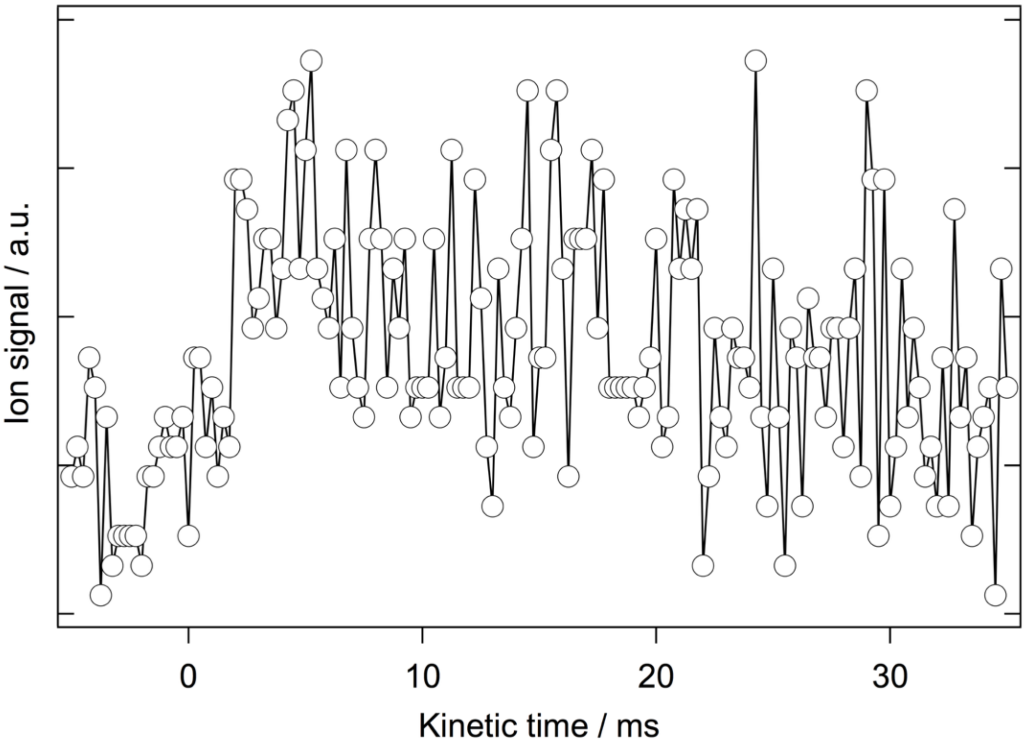

m/z 254 : Acetaldehyde oxide + NO_2, 40 Torr, 300 K, 9.2-9.45 eV
$NO_2 = 5.2 \times 10^{14}$ molecule cm^3

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

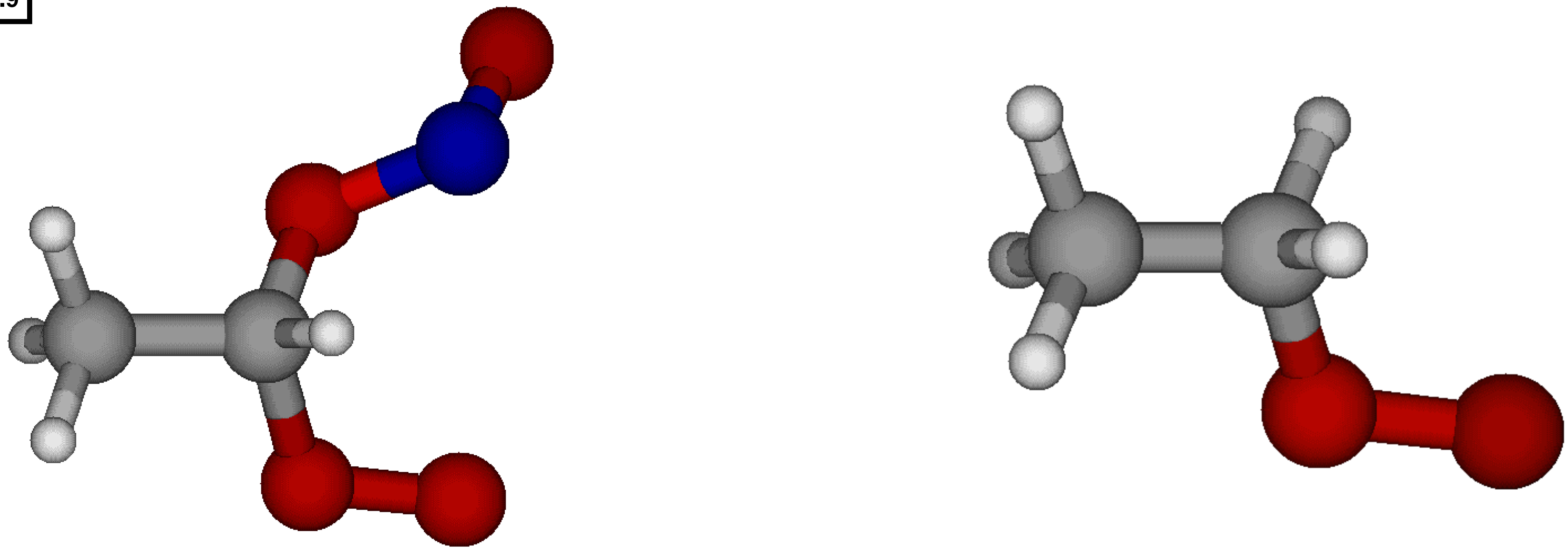
Given the bimolecular rate coefficient for the NO_2 reaction, and the NO_2 concentration are significantly greater than for I + I, **IO + NO_2 is more likely to be the contributing factor to the m/z 189 signal, if it is indeed $IONO_2$.**

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

Geometry comparison between the lowest energy adduct structure and ROO

Fig.9



Isomer # 3

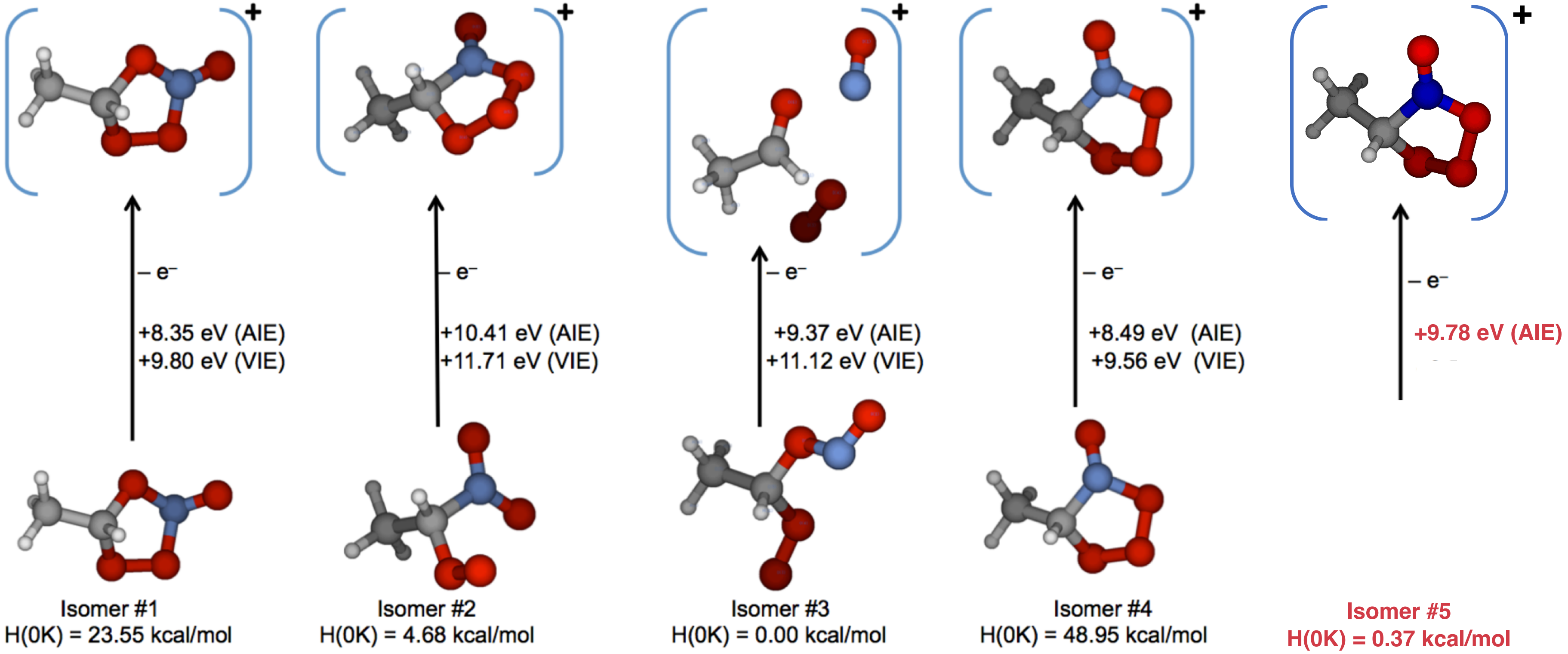
r(O–O) = 1.30 A
r(C–O) = 1.46 A
a(O–O–C) = 111.56 °

Equivalent ROO (H rather than NO_2)

r(O–O) = 1.30 A
r(C–O) = 1.45 A
a(O–O–C) = 111.99 °

Adduct isomer #5

Fig.9



+8.35 eV (AIE)
+9.80 eV (VIE)

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

+10.41 eV (AIE)
+11.71 eV (VIE)

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

+9.37 eV (AIE)
+11.12 eV (VIE)

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

+8.49 eV (AIE)
+9.56 eV (VIE)

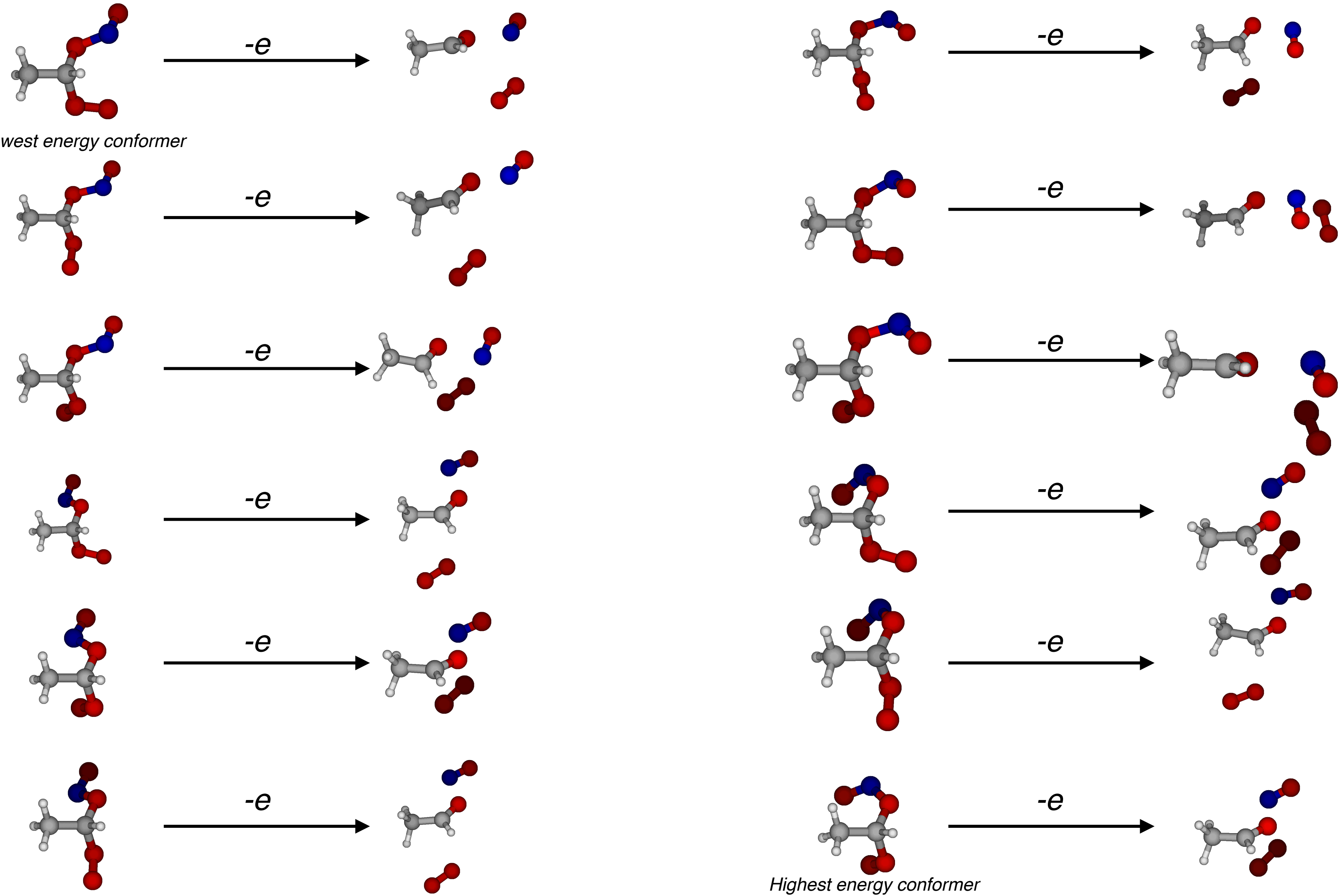
Isomer #4
H(0K) = 48.95 kcal/mol

+9.78 eV (AIE)

Isomer #5
H(0K) = 0.37 kcal/mol

Do all conformers of adduct #3 dissociatively ionize ? - *Yes*

Relaxed scan of conformers of isomer #3 from 0-9.2 kcal/mol relative energy demonstrates all of these conformers dissociatively ionize



Lowest energy conformer

Highest energy conformer