

Supplementary Material for:

Estimation of mechanistic parameters in the gas-phase reactions of ozone with alkenes for use in automated mechanism construction

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Spreadsheet S1: Database of Primary Carbonyl Yields

Note: "carbonyl2" is defined as the most substituted primary carbonyl product

Spreadsheet S2: Database of total SCI yields

Spreadsheet S3: Database of OH yields

Section S1: Fits to determine POZ fragmentation

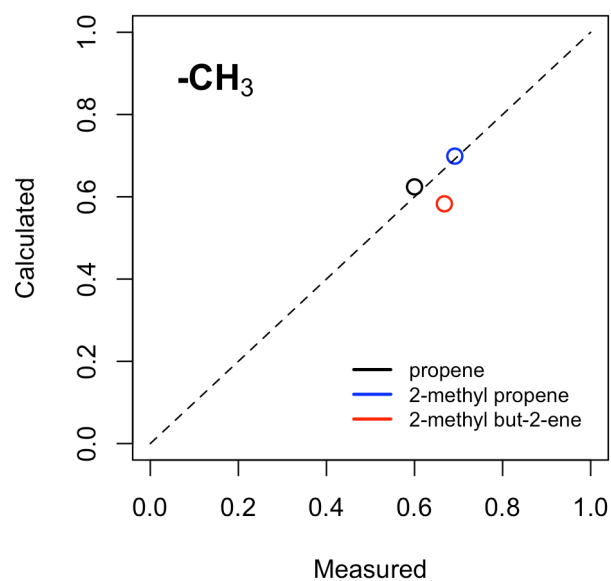


Figure S1: Fit to determine group additivity factor for $-\text{CH}_3$ group in POZ fragmentation.

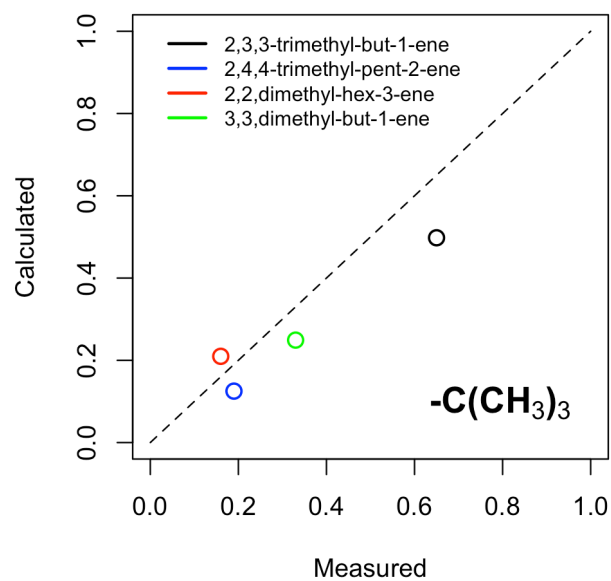


Figure S2: Fit to determine group additivity factor for $-\text{C}(\text{CH}_3)_3$ group in POZ fragmentation.

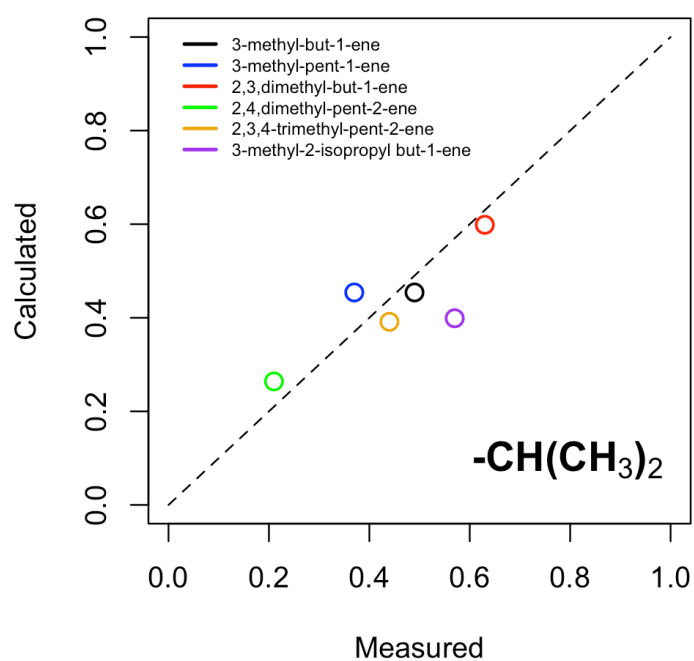


Figure S3: Fit to determine group additivity factor for $-\text{CH}(\text{CH}_3)_2$ group in POZ fragmentation.

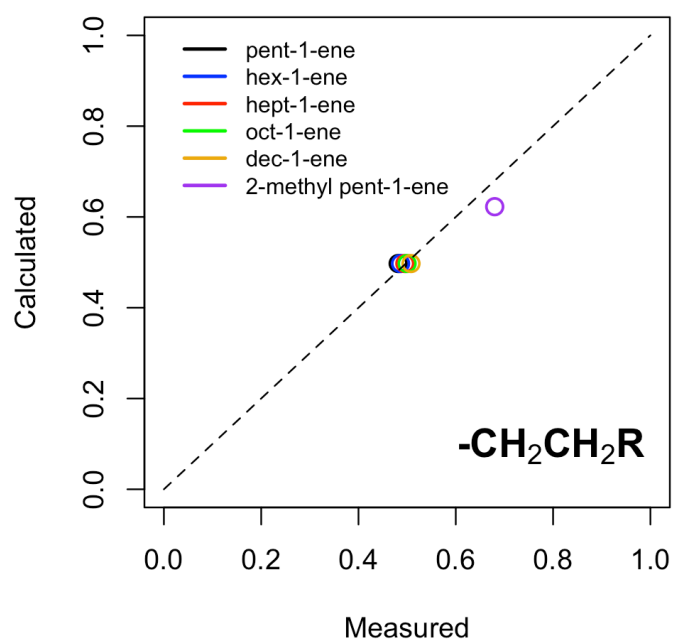


Figure S4: Fit to determine group additivity factor for $-\text{CH}_2\text{CH}_2\text{R}$ group in POZ fragmentation.

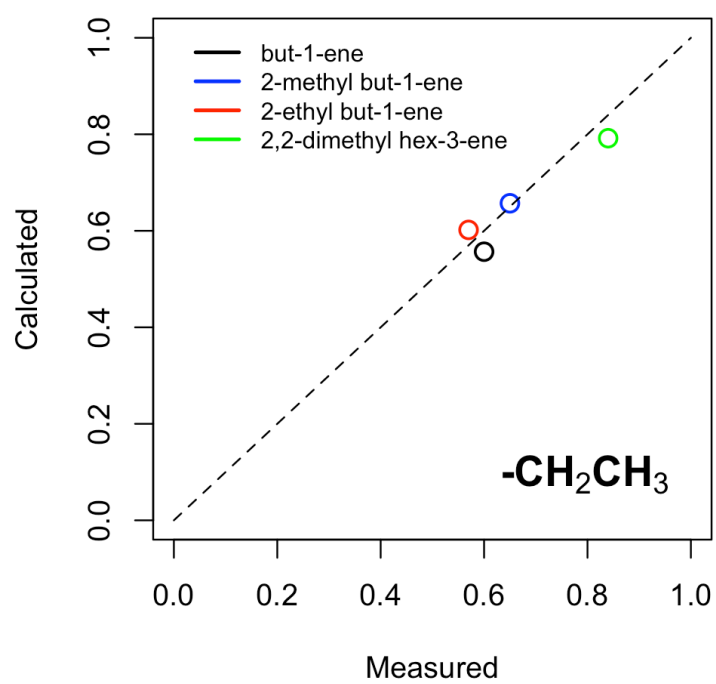


Figure S5: Fit to determine group additivity factor for $-\text{CH}_2\text{CH}_3$ group in POZ fragmentation.

Section S2: Determination of endocyclic alkene SCI yields

An empirically derived fit (Equation S.E1) to the available data for SCI yields of endocyclic alkenes (cyclo-pentene, -hexene, -heptene, methylcyclohexene, α -pinene, limonene, b-caryophyllene).

$$\frac{1}{1+580e^{(-C/2)}} \quad (\text{S.E1})$$

where C = carbon number.

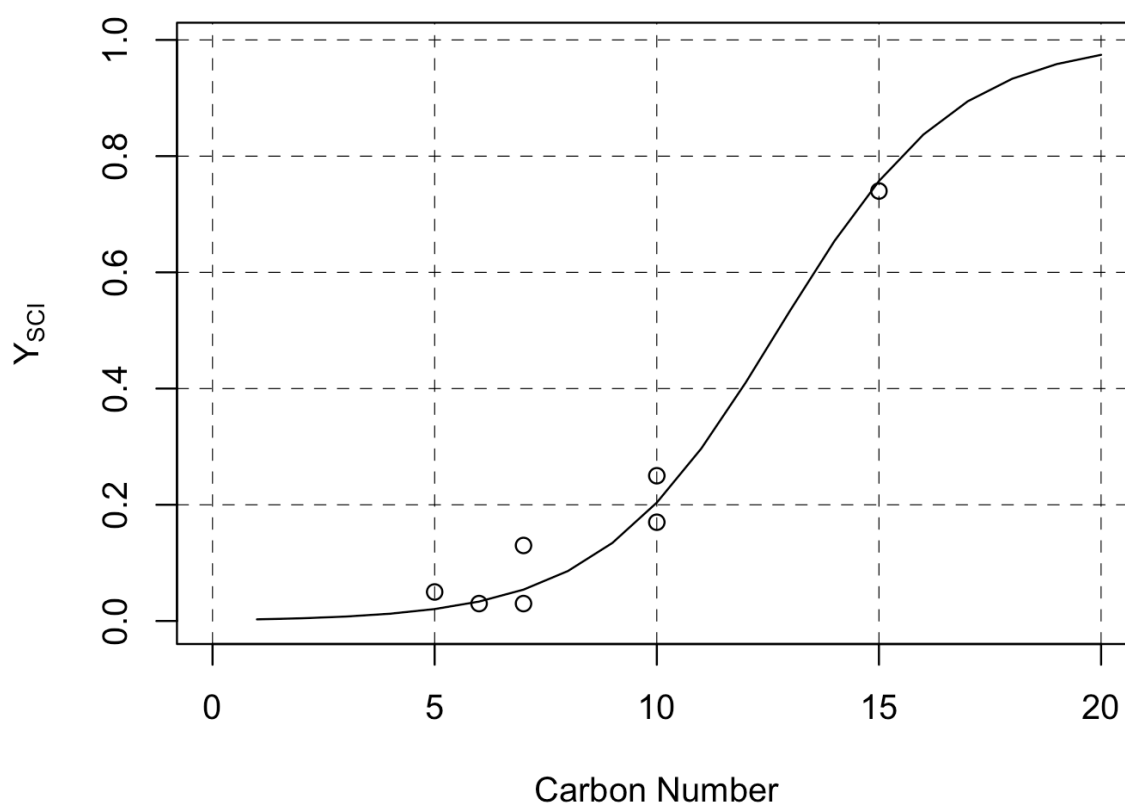
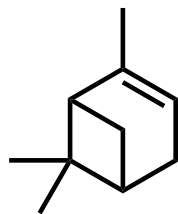


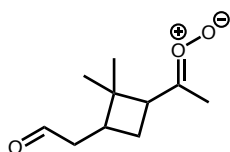
Figure S6. Empirically derived fit to measured SCI yields of endocyclic alkenes.

Section S3: Example Calculations

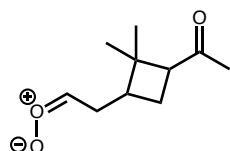
A: α -pinene



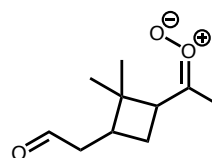
syn-Cl1a:



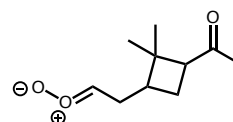
syn-Cl2:



syn-Cl1b:



anti-Cl2:



Cl yields

Treated as $>\text{C}(\text{CH}_3)=\text{CCH}_2\text{CH}_2<$

$$Y_{\text{Cl1}} = \frac{(0.218) - (0+0) + 1}{2} = 0.61 = 1 - Y_{\text{Cl2}}$$

$$Y_{\text{syn-Cl1a}} = 0.61 * 0.5 = 0.30$$

$$Y_{\text{syn-Cl1b}} = 0.61 * 0.5 = 0.30$$

$$Y_{\text{syn-Cl2}} = 0.39 * 0.5 = 0.20$$

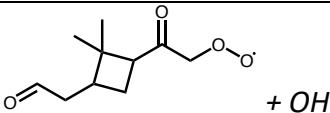
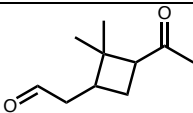
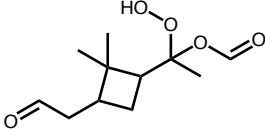
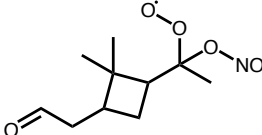
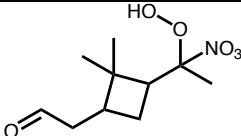
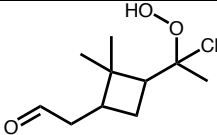
$$Y_{\text{anti-Cl2}} = 0.39 * 0.5 = 0.20$$

*MCM name (mcm.york.ac.uk)

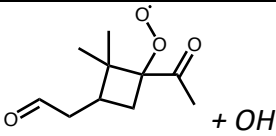
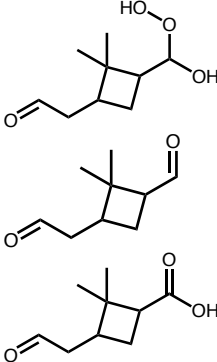
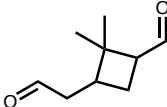
Cl Stabilisation

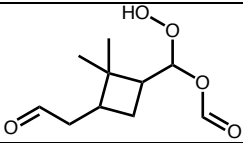
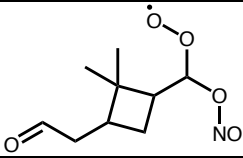
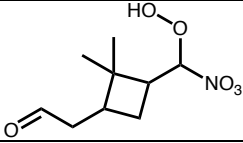
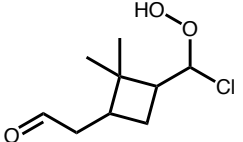
$$S = \frac{1}{1 + 580e^{(-10/2)}} = 0.20$$

syn-CI1a : Decomposition rate, bimolecular rates and products:

Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	611 s^{-1}	 + OH
SO ₂	1.6×10^{-10}	
RCOOH	3.1×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

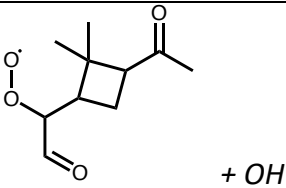
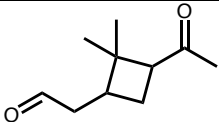
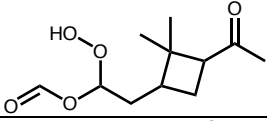
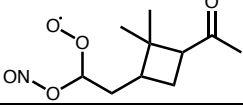
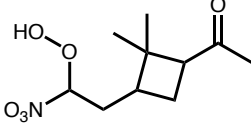
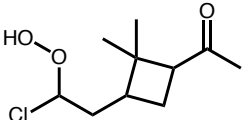
syn-CI1b : Decomposition rate, bimolecular rates and products:

Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	14 s^{-1}	 + OH
H ₂ O (H ₂ O) ₂	9.8×10^{-18} 1.9×10^{-14}	
SO ₂	1.6×10^{-10}	

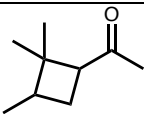
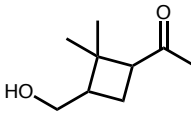
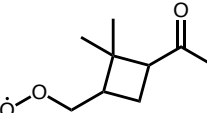
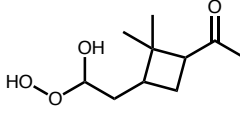
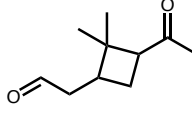
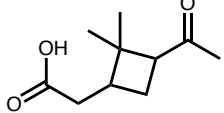
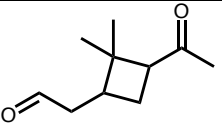
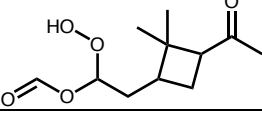
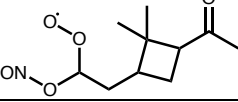
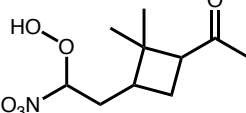
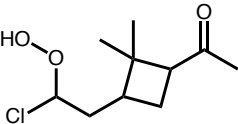
RCOOH	3.1×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

syn-Cl2 : Decomposition rate, bimolecular rates and products

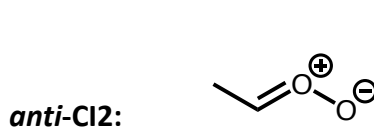
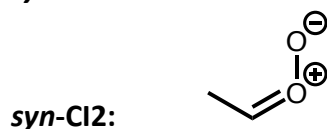
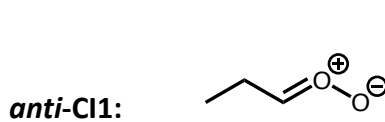
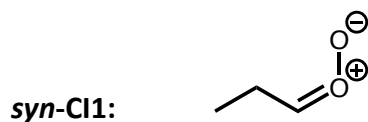
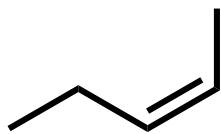
Decomposition rate, bimolecular rates and products:

Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	205 s^{-1}	
SO ₂	2.6×10^{-11}	
RCOOH	2.1×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

anti-Cl2: Decomposition rate, bimolecular rates and products

Reaction Partner	Rate / $\text{cm}^{-3}\text{s}^{-1}$	Products
Unimol.	74 s^{-1}	<div>0.4</div>  <div>0.2</div>  <div>0.4</div> 
$\text{H}_2\text{O} /$ $(\text{H}_2\text{O})_2$	1.6×10^{-14} 1.75×10^{-11}	<div>0.55</div>  <div>0.40</div>  <div>0.05</div> 
SO_2	$1.4 \times 10^{-10} \text{ cm}^{-3}\text{s}^{-1}$	
RCOOH	$3.8 \times 10^{-10} \text{ cm}^{-3}\text{s}^{-1}$	
NO_2	$2 \times 10^{-12} \text{ cm}^{-3}\text{s}^{-1}$	
HNO_3	$5.4 \times 10^{-10} \text{ cm}^{-3}\text{s}^{-1}$	
HCl	$4.6 \times 10^{-11} \text{ cm}^{-3}\text{s}^{-1}$	

B: cis-2-pentene



Cl yields

$$Y_{Cl1} = \frac{(0.218+0)-(0.107+0)+1}{2} = 0.56 = 1 - Y_{Cl2}$$

$$Y_{\text{syn-Cl1}+\text{CH}_3\text{CHO}} = 0.56 * 0.3 = 0.17$$

(*syn:anti* ratio = 0.3:0.7 from *cis*-alkenes)

$$Y_{\text{anti-Cl1}+\text{CH}_3\text{CHO}} = 0.56 * 0.7 = 0.39$$

$$Y_{\text{syn-Cl2}+\text{C}_2\text{H}_5\text{CHO}} = 0.44 * 0.3 = 0.13$$

$$Y_{\text{anti-Cl2}+\text{C}_2\text{H}_5\text{CHO}} = 0.44 * 0.7 = 0.31$$

Cl Stabilisation

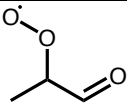
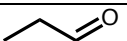
$$(Z)\text{-CH}_3\text{CHOO:} \quad S = 1 - \left[\left(\frac{4}{8} \right) \times 1.242 \times \left(\frac{5}{4+(5-5)} \right) \right] = 0.22$$

$$(E)\text{-CH}_3\text{CHOO:} \quad S = 1 - \left[\left(\frac{4}{8} \right) \times 0.95 \times \left(\frac{5}{4+(5-3)} \right) \right] = 0.60$$

$$(Z)\text{-CH}_3\text{CH}_2\text{CHOO:} \quad S = 1 - \left[\left(\frac{5}{8} \right) \times 1.242 \times \left(\frac{5}{5+(5-5)} \right) \right] = 0.22$$

$$(E)\text{-CH}_3\text{CH}_2\text{CHOO:} \quad S = 1 - \left[\left(\frac{5}{8} \right) \times 0.95 \times \left(\frac{5}{5+(5-3)} \right) \right] = 0.58$$

syn-Cl1: Decomposition rate, bimolecular rates and products

Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	205 s^{-1}	 + OH
SO ₂	2.6×10^{-11}	

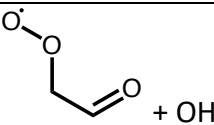

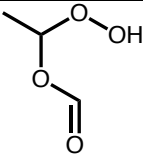
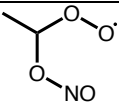
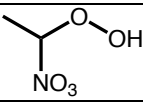
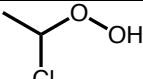
RCOOH	2.1×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

anti-Cl1: Decomposition rate, bimolecular rates and products

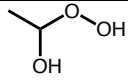



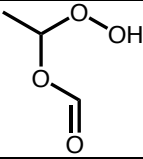
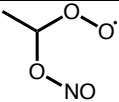
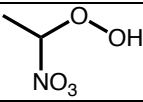
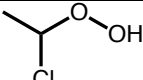
Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	74 s^{-1}	0.4 $\text{C}_2\text{H}_6 + \text{CO}_2$ 0.2 + CO 0.4 + HO ₂ + CO ₂
H ₂ O / (H ₂ O) ₂	1.6×10^{-14} 1.75×10^{-11}	 0.55 0.40 0.05
SO ₂	1.4×10^{-10}	
RCOOH	3.8×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

syn-Cl2: Decomposition rate, bimolecular rates and products

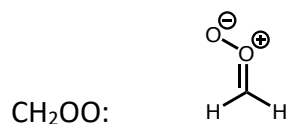
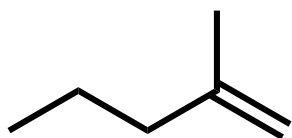
Reaction Partner	Rate / cm^3s^{-1}	Products
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Unimol.	136 s^{-1}	 + OH
SO ₂	2.6×10^{-11}	
RCOOH	2.1×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

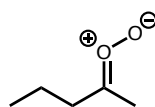
anti-Cl2: Decomposition rate, bimolecular rates and products

Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	53 s^{-1}	0.4 $\text{CH}_4 + \text{CO}_2$ 0.2 $\text{CH}_3\text{OH} + \text{CO}$ 0.4 $\text{CH}_3\text{O}_2 + \text{HO}_2 + \text{CO}_2$
H ₂ O / (H ₂ O) ₂	2.3×10^{-14} 2.7×10^{-11}	0.55  0.40  0.05 
SO ₂	1.4×10^{-10}	
RCOOH	3.8×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

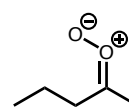
C: 2-methyl-1-pentene



syn-Cl1:



anti-Cl1:



CI yields

$$Y_{Cl1} = \frac{(0.218-0)+1}{2} = 0.61 = 1 - Y_{Cl2}$$

$$Y_{\text{syn-Cl1}+\text{HCHO}} = 0.61 \times 0.5 = 0.30$$

$$Y_{\text{anti-Cl1}+\text{HCHO}} = 0.61 \times 0.5 = 0.30$$

$$Y_{\text{CH}_2\text{OO}+\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{CH}_3} = 1 - 0.61 = 0.39$$

CI Stabilisation

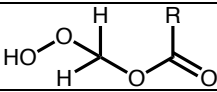
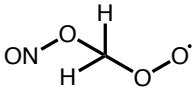
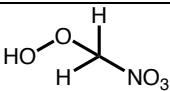
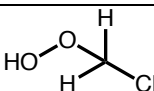
$$\text{CH}_2\text{OO:} \quad S = 1 - \left[\left(\frac{3}{9} \right) \times 0.95 \times \left(\frac{5}{3+(5-3)} \right) \right] = 0.68$$

$$(Z)\text{-CH}_3\text{COO}(\text{CH}_2)_2\text{CH}_3: \quad S = 1 - \left[\left(\frac{7}{9} \right) \times 1.242 \times \left(\frac{5}{7+(5-5)} \right) \right] = 0.31$$

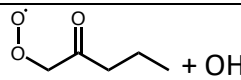
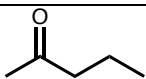
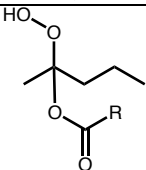
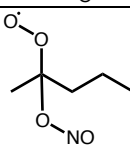
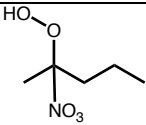
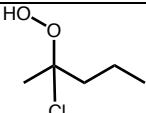
$$(E)\text{-CH}_3\text{COO}(\text{CH}_2)_2\text{CH}_3: \quad S = 1 - \left[\left(\frac{7}{9} \right) \times 0.95 \times \left(\frac{5}{7+(5-3)} \right) \right] = 0.59$$

CH₂OO: Decomposition rate, bimolecular rates and products

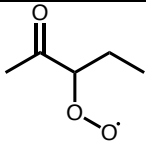
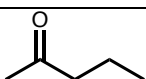
Reaction Partner	Rate / cm ³ s ⁻¹	Products
H ₂ O (H ₂ O) ₂	8.7 × 10 ⁻¹⁶ 1.4 × 10 ⁻¹²	<div>0.55 </div> <div>0.40 </div> <div>0.05 </div>
SO ₂	3.7 × 10 ⁻¹¹	

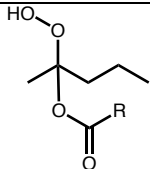
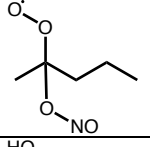
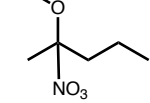
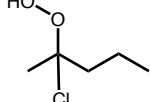
RCOOH	1.2×10^{-10}	
NO ₂	3×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

syn-Cl1: Decomposition rate, bimolecular rates and products

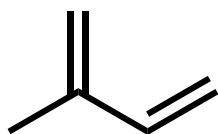
Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	433 s^{-1}	 + OH
SO ₂	1.6×10^{-10}	
RCOOH	3.1×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

anti-Cl1: Decomposition rate, bimolecular rates and products

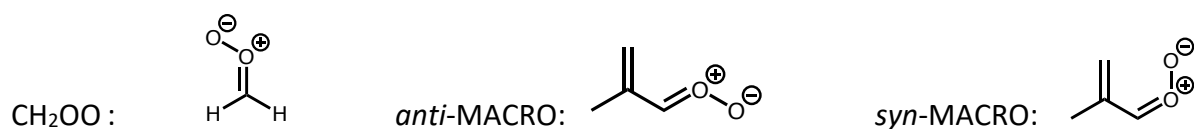
Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	689 s^{-1}	 + OH
SO ₂	1.6×10^{-10}	

RCOOH	3.1×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

D: 2-methyl-1,3-butadiene (Isoprene)



Reaction at terminal double bond: Branching = 0.6 (from Jenkin et al., 2020)



CI yields

$$Y_{CI1} = \frac{(-0.28) - (0) + 1}{2} = 0.36 = 1 - Y_{CI2}$$

$$Y_{\text{anti-MACRO}+\text{HCHO}} = 0.36 \times 0.8 = 0.29 \quad (\text{syn:anti formed with a ratio of 0.2:0.8} - \text{Kuwata et al., 2005})$$

$$Y_{\text{syn-MACRO}+\text{HCHO}} = 0.36 \times 0.2 = 0.07$$

$$Y_{\text{CH}_2\text{OO}+\text{MACR}} = 1 - 0.36 = 0.64$$

CI stabilisation

$$\text{CH}_2\text{OO:} \quad S = 1 - \left[\left(\frac{3}{8} \right) \times 0.95 \times \left(\frac{5}{3+(5-3)} \right) \right] = 0.64$$

$$(Z)\text{-MACRO} \quad S = 1 - \left[\left(\frac{6}{8} \right) \times 1.242 \times \left(\frac{5}{6+(5-5)} \right) \right] = 0.22$$

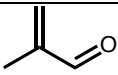
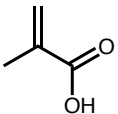
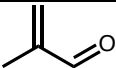
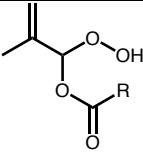
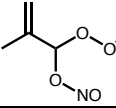
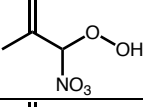
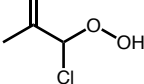
$$(E)\text{-MACRO:} \quad S = 1 - \left[\left(\frac{6}{8} \right) \times 0.95 \times \left(\frac{5}{6+(5-3)} \right) \right] = 0.55$$

CH₂OO: Decomposition rate, bimolecular rates and products

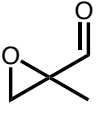
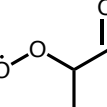
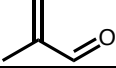
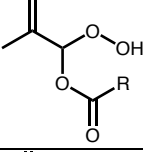
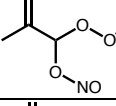
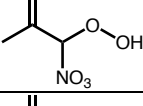
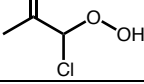
See C: 2-methyl-1-pentene

anti-MACRO (E-(C(CH₃)=CH₂)CHOO): Decomposition rate, bimolecular rates and products

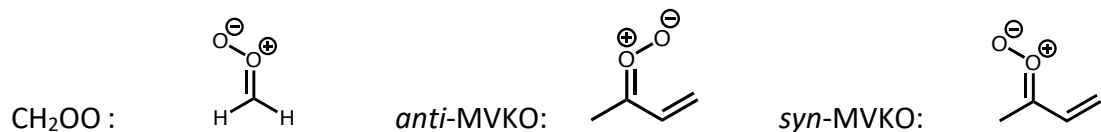
Reaction Partner	Rate / cm ³ s ⁻¹	Products
Unimol.	30 s ⁻¹	0.4 + CO ₂ 0.2 + CO 0.4 + HO ₂ + CO ₂
H ₂ O / (H ₂ O) ₂	1.4 × 10 ⁻¹⁶ 2.7 × 10 ⁻¹³	 0.55

		<div>0.40</div>  <div>0.05</div> 
SO ₂	1.4×10^{-10}	
RCOOH	3.8×10^{-10}	
NO ₂	2×10^{-12}	
HNO ₃	5.4×10^{-10}	
HCl	4.6×10^{-11}	

syn-MACRO (*Z*-(C(CH₃)=CH₂)CHOO): *Decomposition rate, bimolecular rates and products*

Reaction Partner	Rate / cm^3s^{-1}	Products
Unimol.	$13,400 \text{ s}^{-1}$	<div>0.5</div>  <div>0.5</div>  <div>+HCO</div>
SO ₂	$2.6 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$	
RCOOH	$2.1 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$	
NO ₂	$2 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$	
HNO ₃	$5.4 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$	
HCl	$4.6 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$	

Reaction at disubstituted double bond: Branching = 0.4 (from Jenkin et al., 2020)



CI yields

$$Y_{\text{Cl1}} = \frac{(0.218 + -0.28) + 1}{2} = 0.47 = 1 - Y_{\text{Cl2}}$$

$$Y_{\text{anti-MVKO+HCHO}} = 0.47 \times 0.5 = 0.23$$

$$Y_{\text{syn-MVKO+HCHO}} = 0.47 \times 0.5 = 0.23$$

$$Y_{\text{CH}_2\text{OO+MVK}} = 1 - 0.47 = 0.53$$

CI stabilisation

$$\text{CH}_2\text{OO:} \quad S = 1 - \left[\left(\frac{3}{8} \right) \times 0.95 \times \left(\frac{5}{3 + (5-3)} \right) \right] = 0.64$$

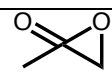
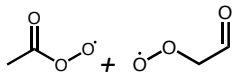
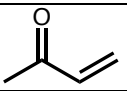
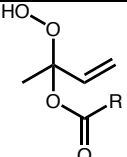
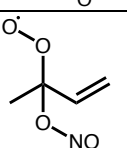
$$\text{anti-MVKO:} \quad S = 1 - \left[\left(\frac{6}{8} \right) \times 1.242 \times \left(\frac{5}{6 + (5-5)} \right) \right] = 0.22$$

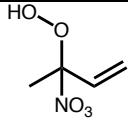
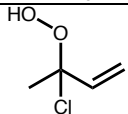
$$\text{syn-MVKO:} \quad S = 1 - \left[\left(\frac{6}{8} \right) \times 1.242 \times \left(\frac{5}{6 + (5-5)} \right) \right] = 0.22$$

CH₂OO: Decomposition rate, bimolecular rates and products

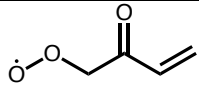
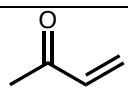
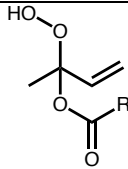
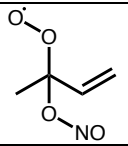
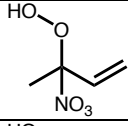
See C: 2-methyl-1-pentene

anti-MVKO (Z-(CH=CH₂)(CH₃)COO): Decomposition rate, bimolecular rates and products

Reaction Partner	Rate / cm ³ s ⁻¹	Products
Unimol.	13,400 s ⁻¹	0.5  0.5 
SO ₂	2.6 × 10 ⁻¹¹ cm ³ s ⁻¹	
RCOOH	2.1 × 10 ⁻¹⁰ cm ³ s ⁻¹	
NO ₂	2 × 10 ⁻¹² cm ³ s ⁻¹	

HNO ₃	$5.4 \times 10^{-10} \text{ cm}^{-3}\text{s}^{-1}$	
HCl	$4.6 \times 10^{-11} \text{ cm}^{-3}\text{s}^{-1}$	

syn-MVKO (*E*-(CH=CH₂)(CH₃)COO): Decomposition rate, bimolecular rates and products

Reaction Partner	Rate / $\text{cm}^{-3}\text{s}^{-1}$	Products
Unimol.	50 s^{-1}	 + OH
SO ₂	$2.6 \times 10^{-11} \text{ cm}^{-3}\text{s}^{-1}$	
RCOOH	$2.1 \times 10^{-10} \text{ cm}^{-3}\text{s}^{-1}$	
NO ₂	$2 \times 10^{-12} \text{ cm}^{-3}\text{s}^{-1}$	
HNO ₃	$5.4 \times 10^{-10} \text{ cm}^{-3}\text{s}^{-1}$	
HCl	$4.6 \times 10^{-11} \text{ cm}^{-3}\text{s}^{-1}$	