

# A Comparison of Chemical Mechanisms using Tagged Ozone Production Potential (TOPP) Analysis: Supplementary Material

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## S1 Introduction

This is the supplementary material to the research paper “A Comparison of Chemical Mechanisms using Tagged Ozone Production Potential (TOPP) Analysis” and provides further information about the methodology as well as additional analysis.

## S2 Mechanism Setup

All chemical mechanisms were adapted from their original format into the modularised KPP (Damian et al., 2002) format for use in the MECCA boxmodel (Sander et al., 2005) as modified by (Butler et al., 2011).

The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2014) is the reference mechanism and its approach to dry deposition, photolysis and peroxy radical–peroxy radical reactions were applied to all mechanisms.

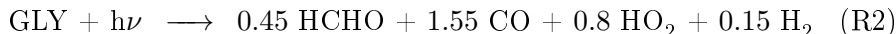
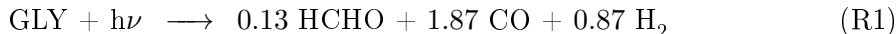
### S2.1 Photolysis

Photolysis was parameterised as a function of the solar zenith angle following the MCM approach (Saunders et al., 2003). Species from reduced mechanisms with a direct

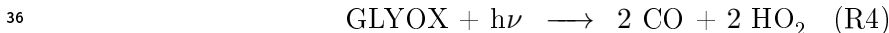
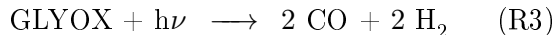
counterpart in the MCM v3.2 were assigned the corresponding MCM v3.2 photolysis rate  
 22 parameter. Otherwise, the recommended rate parameter in the mechanism determined the  
 appropriate MCM v3.2 photolysis rate parameter. In some cases, the MCM v3.2 photolysis  
 24 rate parameter closest in magnitude to that specified by the mechanism.

For example, the organic nitrate species ONIT in RACM2 has a photolysis rate  
 26 parameter of  $1.96 \times 10^{-6} \text{ s}^{-1}$  that was compared to the MCM v3.2 organic nitrate photolysis  
 rate parameters ( $J_{51} - J_{57}$ ). The rate parameter  $J_{54}$  is the most similar in magnitude and  
 28 was assigned as the ONIT photolysis rate parameter in RACM2.

Photolysis reactions of a species in reduced mechanisms were sometimes represented  
 30 by more than one MCM v3.2 photolysis reaction. The product yields of the original  
 mechanism reactions were preserved using combinations of the MCM v3.2 rate parameters.  
 32 For example, glyoxal photolysis described by (R1) and (R2) in RADM2.



34 Whereas in the MCM v3.2, (R3), (R4) and (R5) are prescribed for glyoxal photolysis with  
 the rates  $J_{31}$ ,  $J_{32}$  and  $J_{33}$  respectively.



The product yields in (R1) were retained using a photolysis rate parameter of  
 38  $0.87 J_{31} + 0.13 J_{32}$ , whilst for (R2) the rate  $0.15 J_{31} + 0.45 J_{32} + 0.4 J_{33}$  was used.  
 Table S1 illustrates the product yield calculations.

## 40 **S2.2 Organic Peroxy Radical Self and Cross Reactions**

Reactions of organic peroxy radicals ( $\text{RO}_2$ ) with other organic peroxy radicals are  
 42 divided into self ( $\text{RO}_2 + \text{RO}_2$ ) and cross ( $\text{RO}_2 + \text{R}'\text{O}_2$ ) reactions. These reactions are  
 typically represented in chemical mechanisms as bimolecular reactions which would cause  
 44 ambiguities when implementing the tagging scheme. Namely, which tag to be used for  
 the products of reactions between  $\text{RO}_2$  reactants having different tags. The MCM v3.2  
 46 approach to self and cross  $\text{RO}_2$  reactions (each  $\text{RO}_2$  species reacts with the pool of all

	Rate Parameter	MCM v3.2 Products and Yields
(R1)	0.87 J <sub>31</sub>	1.74 CO + 0.87 H <sub>2</sub>
	0.13 J <sub>32</sub>	0.13 CO + 0.13 HCHO
	0.87 J <sub>31</sub> + 0.13 J <sub>32</sub>	1.87 CO + 0.13 HCHO + 0.87 H <sub>2</sub>
(R2)	0.15 J <sub>31</sub>	0.30 CO + 0.15 H <sub>2</sub>
	0.45 J <sub>32</sub>	0.45 CO + 0.45 HCHO
	0.4 J <sub>33</sub>	0.80 CO + 0.80 HO <sub>2</sub>
	0.15 J <sub>31</sub> + 0.45 J <sub>32</sub> + 0.4 J <sub>33</sub>	1.55 CO + 0.45 HCHO + 0.80 HO <sub>2</sub> + 0.15 H <sub>2</sub>

Table S1: Calculation of glyoxal MCM v3.2 photolysis rate parameters retaining RADM2 glyoxal photolysis product yields.

Mechanism	Reaction	Rate Constant
MCM v3.2	C2H5O2 = C2H5O	$k^*RO2*0.6 \text{ s}^{-1}$
	C2H5O2 = C2H5OH	$k^*RO2*0.2 \text{ s}^{-1}$
	C2H5O2 = CH3CHO	$k^*RO2*0.2 \text{ s}^{-1}$
MOZART-4	C2H5O2 + CH3O2 = 0.7 CH2O + 0.8 CH3CHO + HO2 + 0.3 CH3OH + 0.2 C2H5OH	$2 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
	C2H5O2 + C2H5O2 = 1.6 CH3CHO + 1.2 HO2 + 0.4 C2H5OH	$6.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MOZART-4 modified	C2H5O2 = 0.8 CH3CHO + 0.6 HO2 + 0.2 C2H5OH	$2 \times 10^{-13}*RO2 \text{ s}^{-1}$

Table S2: Ethyl peroxy radical (C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>) self and cross organic peroxy reactions in MCM v3.2 and MOZART-4 including rate constants.  $k = 2(6.6 \times 10^{-27} \exp(365/T))^{\frac{1}{2}} \text{ molecules}^{-1} \text{ s}^{-1}$  and RO2 is the sum of all organic peroxy radical mixing ratios.

Reactants	Products	Rate Constant
MO2 + MO2	0.74 HO2 + 1.37 HCHO + 0.63 MOH	$9.4 \times 10^{-14} \exp(390/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MO2	0.37 HO2 + 0.685 HCHO + 0.315 MOH	$9.4 \times 10^{-14} \exp(390/T)*RO2 \text{ s}^{-1}$
ETHP + MO2	HO2 + 0.75 HCHO + 0.75 ACD + 0.25 MOH + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
ETHP	0.63 HO2 + 0.065 HCHO + 0.75 ACD + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T)*RO2 \text{ s}^{-1}$

Table S3: Dermination of EHP pseudo-unimolecular reaction and rate constant in RACM2 including rate constants. RO2 is the sum of all organic peroxy radical mixing ratios.

other  $\text{RO}_2$  at a single uniform rate) is used to avoid such ambiguities. The MCM v3.2  
 48 approach represents  $\text{RO}_2\text{--RO}_2$  reactions as a pseudo-unimolecular reaction whose rate  
 constant includes a factor ‘RO2’ which is the sum of the mixing ratios of all organic peroxy  
 50 radicals (Saunders et al., 2003).

The pseudo-unimolecular reaction products and their yields were determined by one  
 52 of two methods. Firstly, by using the  $\text{RO}_2 + \text{RO}_2$  reaction and halving the product  
 yields, demonstrated for the MOZART-4 treatment of the ethyl peroxy radical in Table S2.  
 54 Alternatively, the  $\text{RO}_2 + \text{CH}_3\text{O}_2$  reaction was used to determine the products due to  $\text{CH}_3\text{O}_2$   
 and these products are then removed.

56 Table S3 demonstrates the steps determining the ETHP pseudo-unimolecular reaction  
 in RACM2. First the products due to  $\text{MO}_2$  ( $\text{CH}_3\text{O}_2$  in RACM2) are determined as outlined  
 58 previously using the  $\text{MO}_2 + \text{MO}_2$  reaction. The  $\text{MO}_2$  product yields are subtracted from  
 the  $\text{ETHP} + \text{MO}_2$  reaction. Any products having a negative yield are not included in the  
 60 final pseudo-unimolecular reaction.

The methyl acyl peroxy radical ( $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ) was the exception to the above  
 62 approach. Although most mechanisms include a  $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$  reaction,  
 the  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  pseudo-unimolecular reaction was derived by subtracting the  $\text{CH}_3\text{O}_2$   
 64 product yields from the  $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$  reaction. This approach was used as the  
 $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$  reaction is the most significant reaction for  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ .

66 The rate constant for each pseudo-unimolecular reaction was taken as that of the  
 $\text{RO}_2 + \text{CH}_3\text{O}_2$  reaction multiplied by an ‘RO2’ factor, which is the sum of the mixing  
 68 ratios of all organic peroxy radicals. The  $\text{RO}_2 + \text{CH}_3\text{O}_2$  rate constant was chosen as this  
 is the most likely reaction to occur.

70 Model runs using the original and modified approach to the  $\text{RO}_2\text{--RO}_2$  reactions for each  
 mechanism were performed. The resulting  $\text{O}_3$  concentration time series were compared and  
 72 shown in Figure S1.

## S2.3 Dry Deposition

74 Dry deposition velocities are taken from the MCM v3.2. The MCM v3.2 dry deposition  
 velocities of the same chemical functional group were used for mechanism species without  
 76 direct MCM v3.2 analogues. For example, the dry deposition velocity of PAN-like species

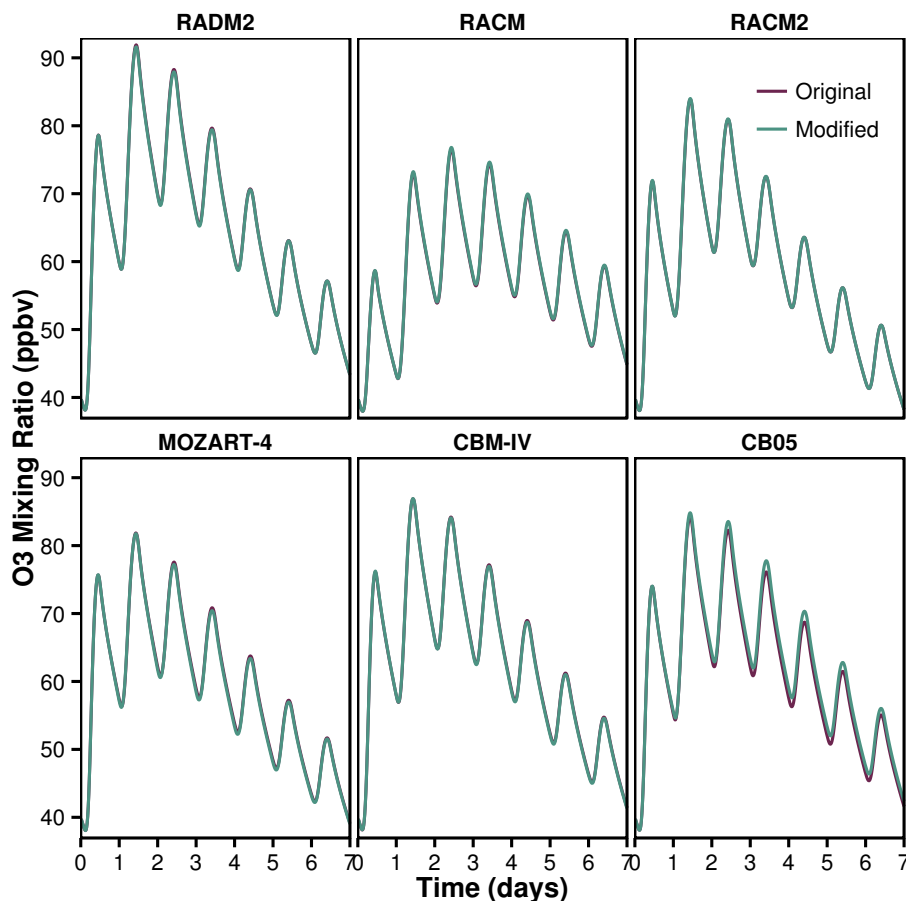


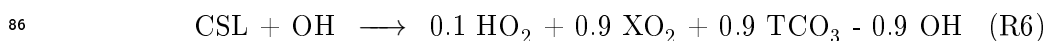
Figure S1: O<sub>3</sub> mixing ratio time series for each reduced mechanism using the original and modified approach to RO<sub>2</sub>-RO<sub>2</sub> reactions

in all mechanisms was equivalent to that of the PAN species in the MCM v3.2.

## 78 S2.4 Negative Product Yield Treatment

Some mechanisms include reactions where products have a negative yield. These reactions  
 80 were re-written including an operator species with a positive yield as the analysis tools  
 used in this study do not allow negative product yields. The operator species acts as a  
 82 sink for the original product by immediately reacting with the original product generating  
 a 'NULL' product.

84 For example, in RADM2 the OH + CSL (cresol) reaction has negative OH yield in  
 (R6) (Stockwell et al., 1990).



The negative OH yield was adapted to a positive operator (OHOP) yield in (R7). OHOP

88 then reacts immediately with OH giving a ‘NULL’ product with a rate constant of  
 $8.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (R8). Thus preserving the OH yields from (R6) in RADM2.



### S3 Mapping Emitted NMVOC to Mechanism Species

92 The emitted NMVOC are typical of Los Angeles as described in Baker et al. (2008). The  
MCM v3.2, v3.1 (Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2003) and CRI v2  
94 (Jenkin et al., 2008) explicitly represent all of these NMVOC.

NMVOC representation in all other mechanisms required mapping to specific  
96 mechanism species. This mapping followed the recommendations on the literature of  
the mechanism. Table S4 describes the mechanism species used for mapping the initial  
98 NMVOC. Table 2 of the main article shows the final mapping of each NMVOC to each  
mechanism species.

Mechanism	Species	Description	Mechanism	Species	Description
MOZART-4 (Emmons et al., 2010)	C2H6	Ethane	RACM2 (Goliff et al., 2013)	ETH	Ethane
	C3H8	Propane		HC3	OH rate constant (298 K, 1 atm) less than $3.4 \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$
	BIGALK	Lumped alkanes C > 3		HC5	OH rate constant (298 K, 1 atm) between $3.4 \times 10^{-12}$ and $6.8 \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$
	C2H4	Ethene		HC8	OH rate constant (298 K, 1 atm) greater than $6.8 \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$
	C3H6	Propene		ETE	Ethene
	BIGENE	Lumped alkenes C > 3		OLT	Terminal alkenes
	ISOP	Isoprene		OLI	Internal alkenes
	TOLUENE	Lumped aromatics		ISO	Isoprene
	ETH	Ethane		BEN	Benzene
	HC3	OH rate constant (298, 1 atm) between $2.7 \times 10^{-13}$ and $3.4 \times 10^{-12}$		TOL	Toluene and less reactive aromatics
RADM2 (Stockwell et al., 1990)	HC5	OH rate constant (298, 1 atm) between $3.4 \times 10^{-12}$ and $6.8 \times 10^{-12}$	CBM-IV (Gery et al., 1989)	XYM	m-Xylene
	HC8	OH rate constant (298, 1 atm) greater than $6.8 \times 10^{-12}$		XYO	o-Xylene
	OL2	Ethene		XYP	p-Xylene
	OLT	Terminal Alkenes		PAR	Paraffin carbon bond C-C
	OLI	Internal Alkenes		ETH	Ethene
	ISO	Isoprene		OLE	Olefinic carbon bond C=C
	TOL	Toluene and less reactive aromatics		ALD2	High molecular weight aldehydes
	XYL	Xylene and more reactive aromatics		ISOP	Isoprene
	ETH	Ethane		TOL	Toluene
	HC3	OH rate constant (298 K, 1 atm) less than $3.4 \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$		XYL	Xylene
RACM (Stockwell et al., 1997)	HC5	OH rate constant (298 K, 1 atm) between $3.4 \times 10^{-12}$ and $6.8 \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$	CB05 (Yarwood et al., 2005)	FORM	Formaldehyde
	HC8	OH rate constant (298 K, 1 atm) greater than $6.8 \times 10^{-12}$		ETHA	Ethane
	ETE	Ethene		PAR	Paraffin carbon bond C-C
	OLT	Terminal alkenes		OLE	Terminal olefin carbon bond R-C=C
	OLI	Internal alkenes		FORM	Formaldehyde
	ISO	Isoprene		ISOP	Isoprene
	TOL	Toluene and less reactive aromatics		TOL	Toluene and other monoalkyl aromatics
	XYL	Xylene and more reactive aromatics		XYL	Xylene and other polyalkyl aromatics
	ETH	Ethane			
	HC3	OH rate constant (298 K, 1 atm) less than $3.4 \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$			

Table S4: Description of primary mechanism species used for mapping emitted NMVOCs.

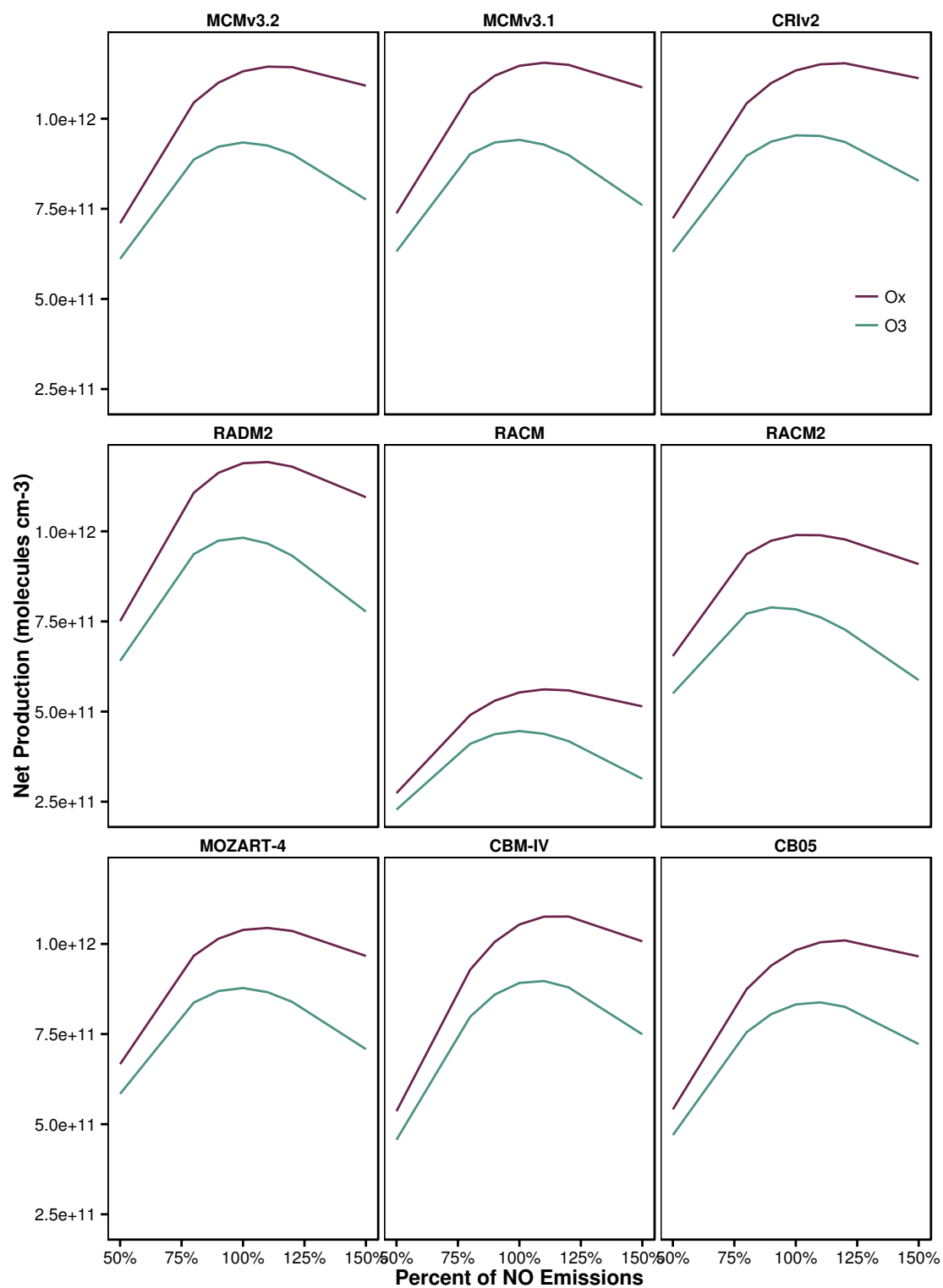


Figure S2: Maximum O<sub>3</sub> and O<sub>x</sub> production on the first day calculated over varying NO emissions to verify that each mechanism is in a state of maximum O<sub>3</sub> production.



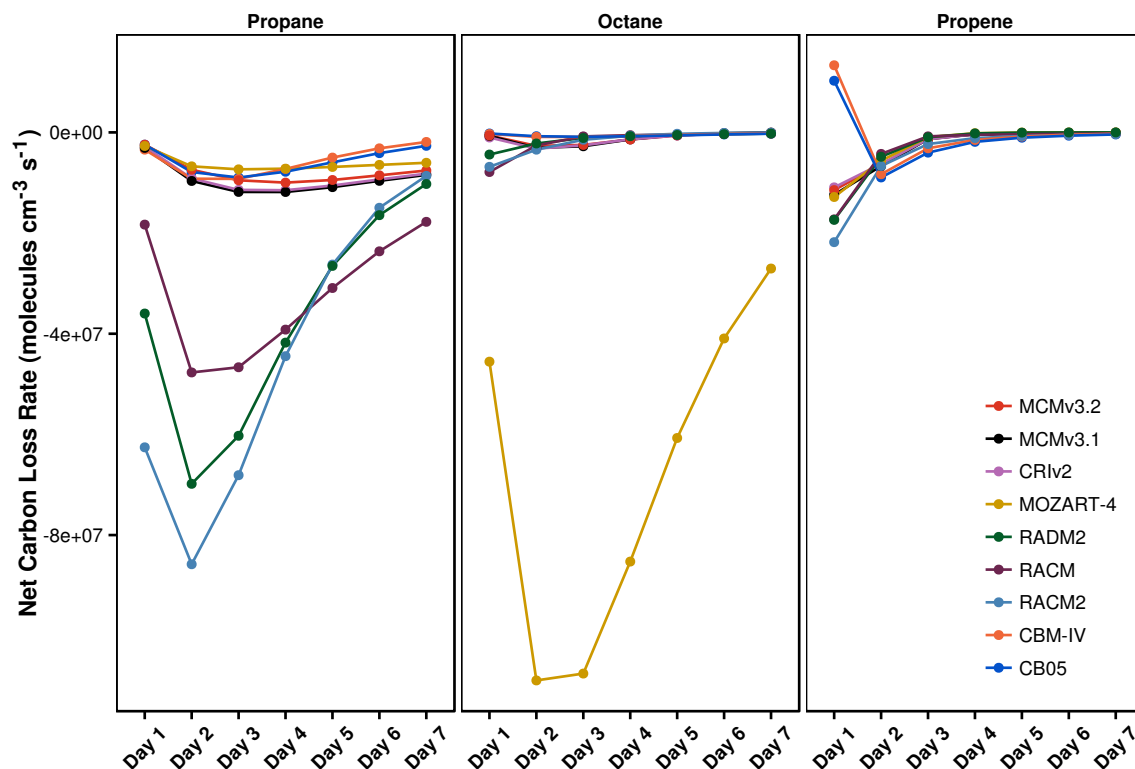


Figure S3: Net loss of reactive carbon during propane, octane and propene degradation in each mechanism. Octane is represented by the 5 carbon species, BIGALK, in MOZART-4.

## References

- Angela K. Baker, Andreas J. Beyersdorf, Lambert A. Doezema, Aaron Katzenstein, Simone Meinardi, Isobel J. Simpson, Donald R. Blake, and F. Sherwood Rowland. Measurements of nonmethane hydrocarbons in 28 United States cities. *Atmospheric Environment*, 42: 170–182, 2008.
- C. Bloss, V. Wagner, M. E. Jenkin, R. Vollamer, W. J. Bloss, J. D. Lee, D. E. Heard, K. Wirtz, M. Martin-Reviejo, G. Rea, J. C. Wenger, and M. J. Pilling. Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons. *Atmospheric Chemistry and Physics*, 5:641–664, 2005.
- T. M. Butler, M. G. Lawrence, D. Taraborrelli, and J. Lelieveld. Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach. *Atmospheric Environment*, 45(24):4082–4090, 2011.

V. Damian, A. Sandu, M. Damian, F. Potra, and G.R. Carmichael. The kinetic

- preprocessor KPP - A software environment for solving chemical kinetics. *Computers and Chemical Engineering*, 26(11):1567–1579, 2002.
- L. K. Emmons, S. Walters, P. G. Hess, J.-F. Lamarque, G. G. Pfister, D. Fillmore, C. Granier, A. Guenther, D. Kinnison, T. Laepple, J. Orlando, X. Tie, G. Tyndall, C. Wiedinmyer, S. L. Baughcum, and S. Kloster. Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4). *Geoscientific Model Development*, 3:43–67, 2010.
- Michael W. Gery, Gary Z. Whitten, James P. Killus, and Marcia C. Dodge. A photochemical kinetics mechanism for urban and regional scale computer modeling. *Journal of Geophysical Research*, 94(D10):12,925–12,956, 1989.
- Wendy S. Goliff, William R. Stockwell, and Charlene V. Lawson. The regional atmospheric chemistry mechanism, version 2. *Atmospheric Environment*, 68:174–185, 2013.
- M. E. Jenkin, S. M. Saunders, V. Wagner, and M. J. Pilling. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, 3(1):181–193, 2003.
- M. E. Jenkin, L. A. Watson, S. R. Utembe, and D. E. Shallcross. A Common Representative Intermediates (CRI) mechanism for VOC degradation. Part 1: Gas phase mechanism development. *Atmospheric Environment*, 42:7185–7195, 2008.
- Michael E. Jenkin, Sandra M. Saunders, and Michael J. Pilling. The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmospheric Environment*, 31(1):81–104, 1997.
- Andrew Rickard, Jenny Young, and Stephen Pascoe. The Master Chemical Mechanism: Major updates in MCM v3.2. [http://mcm.leeds.ac.uk/MCM/project.htm#New\\_3.2](http://mcm.leeds.ac.uk/MCM/project.htm#New_3.2), 2014. [Online; accessed 15-January-2015].
- R. Sander, A. Kerkweg, P. Jöckel, and J. Lelieveld. Technical Note: The new comprehensive atmospheric chemistry module MECCA. *Atmospheric Chemistry and Physics*, 5:445–450, 2005.

- S. M. Saunders, M. E. Jenkin, R. G. Derwent, and M. J. Pilling. Protocol for the  
142 development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric  
degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and*  
144 *Physics*, 3(1):161–180, 2003.
- William R. Stockwell, Paulete Middleton, Julius S. Chang, and Xiaoyan Tang. The Second  
146 Generation Regional Acid Deposition Model Chemical Mechanism for Regional Air Quality  
Modeling. *Journal of Geophysical Research*, 95(D10):16,343–16,367, 1990.
- 148 William R. Stockwell, Frank Kirchner, Michael Kuhn, and Stephan Seefeld. A new  
mechanism for regional atmospheric chemistry modeling. *Journal of Geophysical Research*  
150 *D: Atmospheres*, 102(22):25,847–25,879, 1997.
- Greg Yarwood, Sunja Rao, Mark Yocke, and Gary Z. Whitten. Updates to the Carbon  
152 Bond Chemical Mechanism: CB05. Technical report, U. S Environmental Protection  
Agency, 2005.