

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).

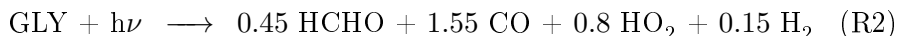
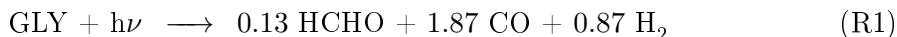
The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2015) is the reference mechanism and its approach to dry deposition, photolysis and peroxy radical–peroxy radical reactions were applied to all mechanisms.

S2.1 Photolysis

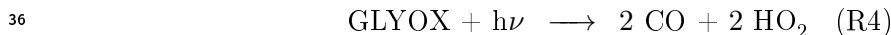
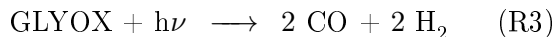
Photolysis was parameterised as a function of the solar zenith angle following the MCM approach (Saunders et al., 2003). Species from reduced mechanisms with a direct

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 was used. For
 example, the organic nitrate species ONIT in RACM2 has a photolysis rate parameter
 26 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 was
 28 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} .



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 (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 RO_2 reactants having different tags. The MCM v3.2
 46 approach to self and cross RO_2 reactions (each RO_2 species reacts with the pool of all

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

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 (C₂H₅O₂) 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 EThP pseudo-unimolecular reaction and rate constant in RACM2 including rate constants. RO2 is the sum of all organic peroxy radical mixing ratios.

other RO_2 at a single uniform rate) is used to avoid such ambiguities. The MCM v3.2
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
radicals (Saunders et al., 2003).

The pseudo-unimolecular reaction products and their yields were determined by one
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.
Alternatively, the $\text{RO}_2 + \text{CH}_3\text{O}_2$ reaction was used to determine the products due to CH_3O_2
and these products are then removed.

Table S3 demonstrates the steps determining the ETHP pseudo-unimolecular reaction
in RACM2. First the products due to MO_2 (CH_3O_2 in RACM2) are determined as outlined
previously using the $\text{MO}_2 + \text{MO}_2$ reaction. The 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
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
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 CH_3O_2
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 $\text{CH}_3\text{C}(\text{O})\text{O}_2$.

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
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.

Model runs using the original and modified approach to the $\text{RO}_2\text{--RO}_2$ reactions for each
mechanism were performed. The resulting O_3 concentration time series were compared and
shown in Figure S1.

S2.3 Dry Deposition

Dry deposition velocities for individual chemical species 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 direct MCM v3.2 analogues. For example, the dry deposition

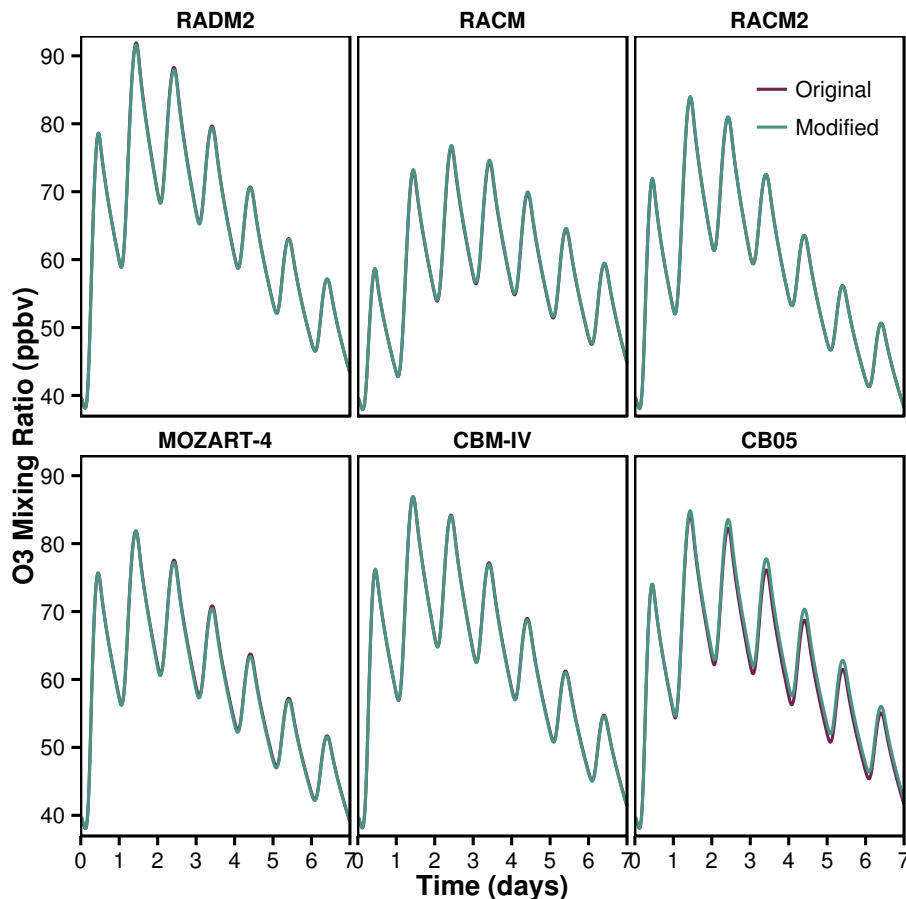


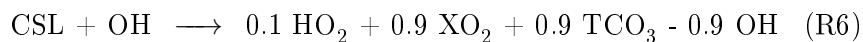
Figure S1: O₃ mixing ratio time series for each reduced mechanism using the original and modified approach to RO₂-RO₂ reactions

velocity of PAN-like species in all mechanisms was equivalent to that of the PAN species
 78 in the MCM v3.2.

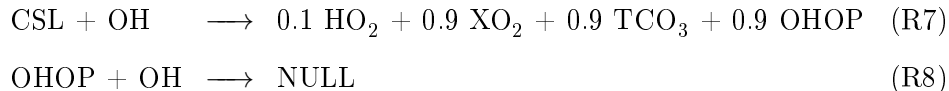
S2.4 Negative Product Yield Treatment

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

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



88 The negative OH yield was adapted to a positive operator (OHOP) yield in (R7). OHOP
then reacts immediately with OH giving a ‘NULL’ product with a rate constant of
90 $8.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (R8). Thus preserving the OH yields from (R6) in RADM2.



92 **S3 Mapping Emitted NMVOC to Mechanism Species**

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

96 NMVOC representation in all other mechanisms required mapping to specific
mechanism species. This mapping followed the recommendations on the literature of
98 the mechanism; Table S4 describes the mechanism species used for mapping the initial
NMVOC. Table 2 of the main article shows the final mapping of each NMVOC to each
100 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 3.4×10^{-12} $\text{cm}^3 \text{s}^{-1}$
	BIGALK	Lumped alkanes C > 3		HC5	OH rate constant (298 K, 1 atm) between 3.4×10^{-12} and 6.8×10^{-12} $\text{cm}^3 \text{s}^{-1}$
	C2H4	Ethene		HC8	OH rate constant (298 K, 1 atm) greater than 6.8×10^{-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 2.7×10^{-13} and 3.4×10^{-12}		TOL	Toluene and less reactive aromatics
RADM2 (Stockwell et al., 1990)	HC5	OH rate constant (298, 1 atm) between 3.4×10^{-12} and 6.8×10^{-12}	CBM-IV (Gery et al., 1989)	XYM	m-Xylene
	HC8	OH rate constant (298, 1 atm) greater than 6.8×10^{-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 3.4×10^{-12} $\text{cm}^3 \text{s}^{-1}$		XYL	Xylene
RACM (Stockwell et al., 1997)	HC5	OH rate constant (298 K, 1 atm) between 3.4×10^{-12} and 6.8×10^{-12} $\text{cm}^3 \text{s}^{-1}$	CB05 (Yarwood et al., 2005)	FORM	Formaldehyde
	HC8	OH rate constant (298 K, 1 atm) greater than 6.8×10^{-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 3.4×10^{-12} $\text{cm}^3 \text{s}^{-1}$			

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

S4 Treatment of 2-methylpropene Degradation

Figure 4 of the main article shows the first day TOPP values of the VOC obtained in each reduced mechanism compared to the MCM v3.2. The first day TOPP values of 2-methylpropene in RACM, RACM2, MOZART-4, CBM-IV and CB05 signify differences in its degradation to the MCM v3.2.

The variation between RACM, RACM2 and MCM v3.2 arises from differences in the ozonolysis rate constant of 2-methylpropene. This rate constant is an order of magnitude faster in RACM and RACM2 than in MCM v3.2 as the RACM, RACM2 rate constant is a weighted mean of the ozonolysis rate constants of each VOC represented as OLI (Stockwell et al., 1997; Goliff et al., 2013). The faster rate constant promotes increased radical production leading to more O_x in RACM and RACM2 than the MCM v3.2.

2-methylpropene is represented as BIGENE in MOZART-4. The degradation of BIGENE produces CH_3CHO through the reaction between NO and the 2-methylpropene peroxy radical, whereas no CH_3CHO is produced during 2-methylpropene degradation in the MCM v3.2. CH_3CHO initiates a degradation chain producing O_x involving CH_3CO_3 and CH_3O_2 leading to more O_x in MOZART-4 than MCM v3.2.

CBM-IV and CB05 represent 2-methylpropene as a combination of aldehydes and PAR, the C–C bond (Gery et al., 1989; Yarwood et al., 2005). This representation of 2-methylpropene does not produce the 2-methylpropene peroxy radical, whose reaction with NO is the main source of O_x production in all other mechanisms.

S5 Extra Plots

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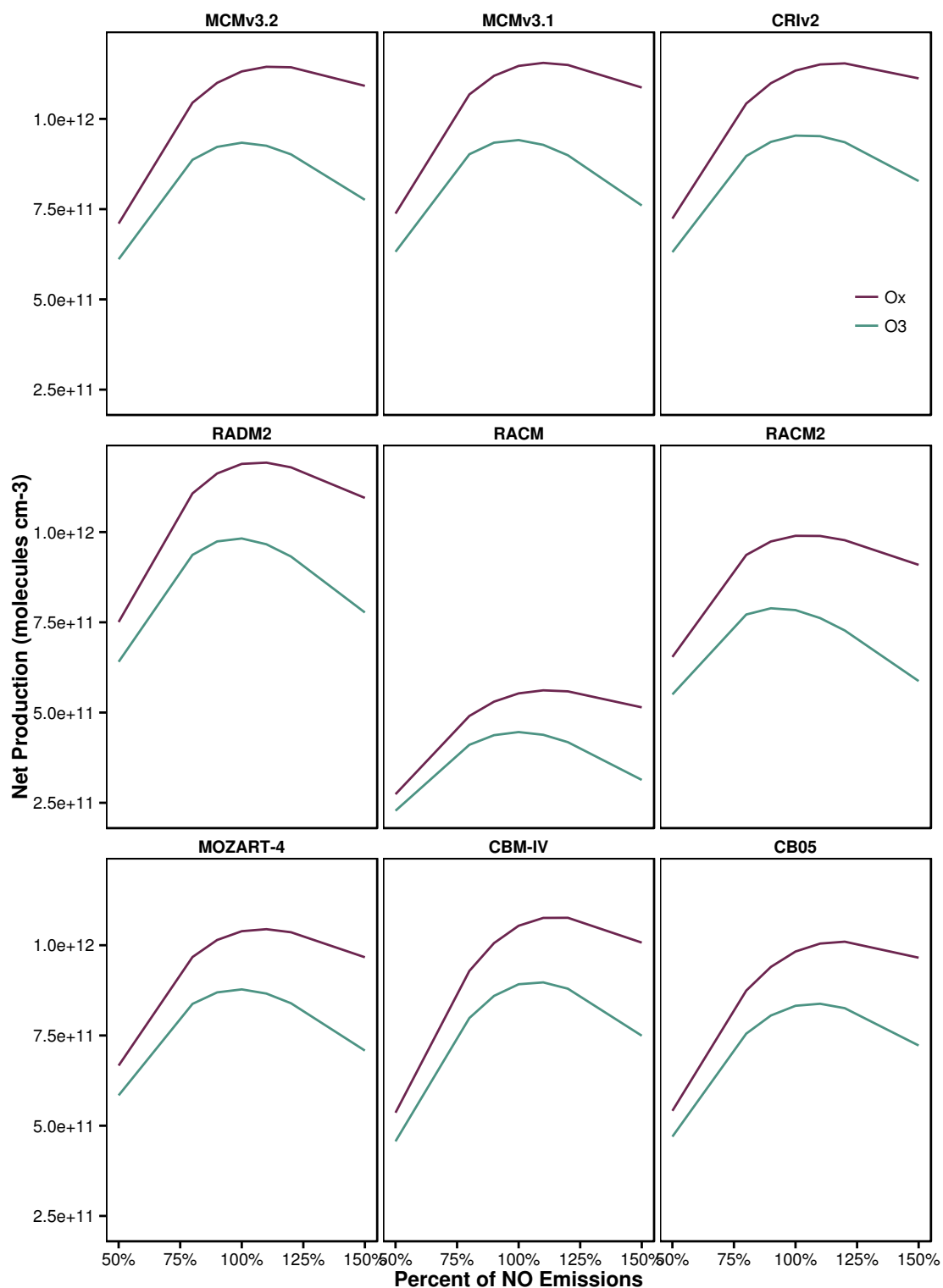


Figure S2: Maximum O_3 and O_x production on the first day calculated over varying NO emissions to verify that each mechanism is in a state of maximum O_3 production.

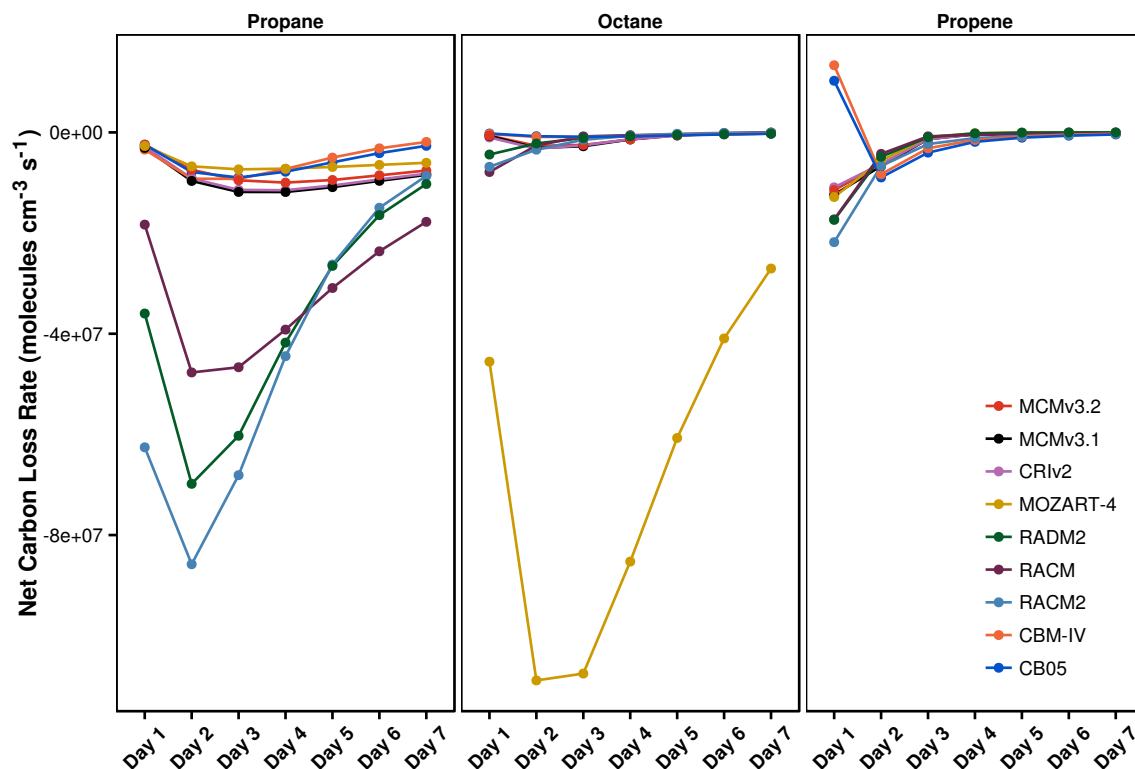


Figure S3: Net loss of reactive carbon during propane, octane and propene degradation in each mechanism. Octane is represented by the 5 carbon species, BIGALK, in MOZART-4.

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