

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

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March 19, 2015

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).

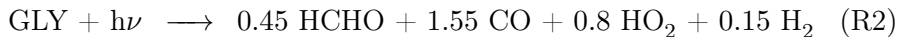
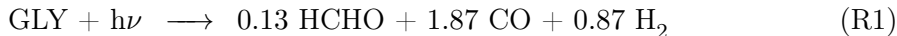
The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2015) is the reference mechanism and its approach to dry deposition, photolysis and peroxy radical–peroxy radical reactions were applied to all mechanisms.

S2.1 Photolysis

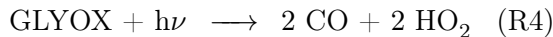
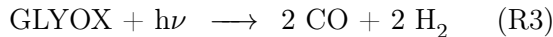
Photolysis was parameterised as a function of the solar zenith angle following the MCM approach (Saunders et al., 2003). Species from reduced mechanisms with a direct counterpart

in the MCM v3.2 were assigned the corresponding MCM v3.2 photolysis rate 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 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 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 assigned as the ONIT photolysis rate parameter in RACM2.

Photolysis reactions of a species in reduced mechanisms were sometimes represented 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. For example, glyoxal photolysis described by (R1) and (R2) in RADM2.



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 $0.87 J_{31} + 0.13 J_{32}$, 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.

S2.2 Organic Peroxy Radical Self and Cross Reactions

Reactions of organic peroxy radicals (RO_2) with other organic peroxy radicals are 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 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 approach to self and cross RO_2 reactions (each RO_2 species reacts with the pool of all other RO_2 at a

	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	C ₂ H ₅ O ₂ = C ₂ H ₅ O	$k^*RO_2*0.6 \text{ s}^{-1}$
	C ₂ H ₅ O ₂ = C ₂ H ₅ OH	$k^*RO_2*0.2 \text{ s}^{-1}$
	C ₂ H ₅ O ₂ = CH ₃ CHO	$k^*RO_2*0.2 \text{ s}^{-1}$
MOZART-4	C ₂ H ₅ O ₂ + CH ₃ O ₂ = 0.7 CH ₂ O + 0.8 CH ₃ CHO + HO ₂ + 0.3 CH ₃ OH + 0.2 C ₂ H ₅ OH	$2 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
	C ₂ H ₅ O ₂ + C ₂ H ₅ O ₂ = 1.6 CH ₃ CHO + 1.2 HO ₂ + 0.4 C ₂ H ₅ OH	$6.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MOZART-4 modified	C ₂ H ₅ O ₂ = 0.8 CH ₃ CHO + 0.6 HO ₂ + 0.2 C ₂ H ₅ OH	$2 \times 10^{-13}*RO_2 \text{ s}^{-1}$

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
MO ₂ + MO ₂	0.74 HO ₂ + 1.37 HCHO + 0.63 MOH	$9.4 \times 10^{-14} \exp(390/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MO ₂	0.37 HO ₂ + 0.685 HCHO + 0.315 MOH	$9.4 \times 10^{-14} \exp(390/T)*RO_2 \text{ s}^{-1}$
ETHP + MO ₂	HO ₂ + 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 HO ₂ + 0.065 HCHO + 0.75 ACD + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T)*RO_2 \text{ s}^{-1}$

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.

single uniform rate) is used to avoid such ambiguities. The MCM v3.2 approach represents
48 $\text{RO}_2\text{--RO}_2$ 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.,
50 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 CH_3O_2
and these products are then removed.

56 Table S3 demonstrates the steps determining the EHP pseudo-unimolecular reaction
in RACM2. First the products due to MO_2 (CH_3O_2 in RACM2) are determined as outlined
58 previously using the $\text{MO}_2 + \text{MO}_2$ reaction. The MO_2 product yields are subtracted from
the EHP + 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 approach.
62 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
64 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 ratios
68 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 O_3 concentration time series were compared
72 and shown in Figure S1.

S2.3 Dry Deposition

74 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
76 mechanism species without direct MCM v3.2 analogues. For example, the dry deposition

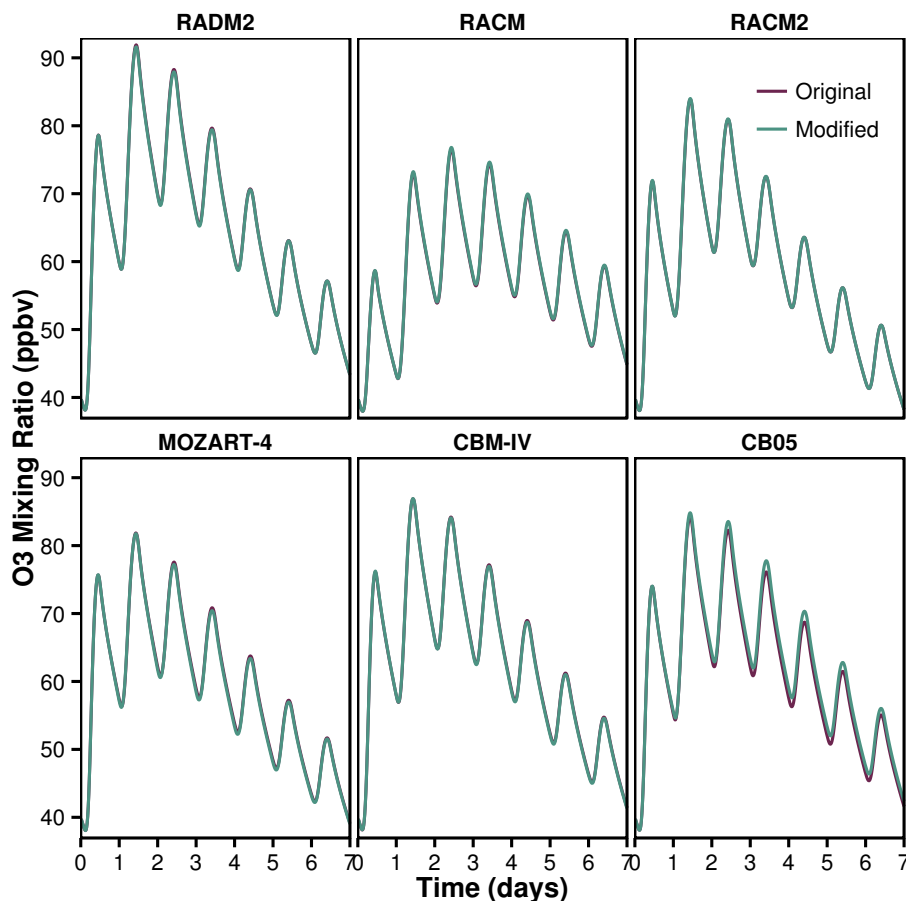


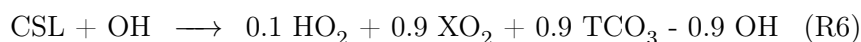
Figure S1: O₃ mixing ratio time series for each reduced mechanism using the original and modified approach to RO₂-RO₂ reactions

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

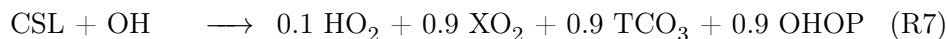
S2.4 Negative Product Yield Treatment

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 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 a 'NULL' product.

For example, in RADM2 the OH + CSL (cresol) reaction has negative OH yield in (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 the mechanism;
98 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 mechanism species.

100 **S4 Treatment of 2-methylpropene Degradation**

Figure 4 of the main article shows the first day TOPP values of the VOC obtained in
102 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
104 in its degradation to the MCM v3.2.

The variation between RACM, RACM2 and MCM v3.2 arises from differences in the
106 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
108 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
110 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
112 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
114 v3.2. CH_3CHO initiates a degradation chain producing O_x involving CH_3CO_3 and CH_3O_2

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 $6.8 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$
	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 2.7×10^{-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 $3.4 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$		XYL	Xylene
RACM (Stockwell et al., 1997)	HC5	OH rate constant (298 K, 1 atm) between 3.4×10^{-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 6.8×10^{-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.

leading to more O_x in MOZART-4 than MCM v3.2.

116 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
 118 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.

120 S5 Extra Plots

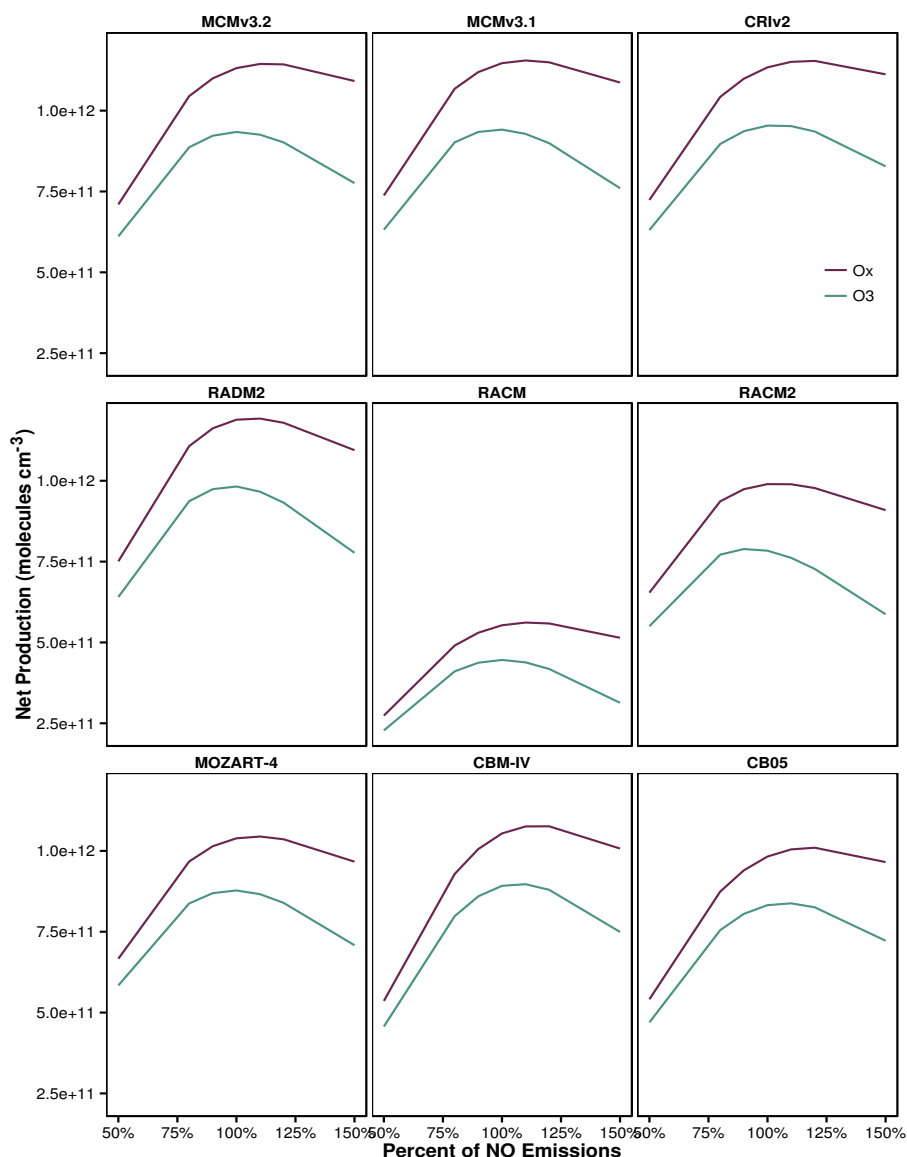


Figure S2: Maximum O_3 and O_x production on the first day calculated over varying NO emissions to verify that each mechanism is in a state of maximum O_3 production.

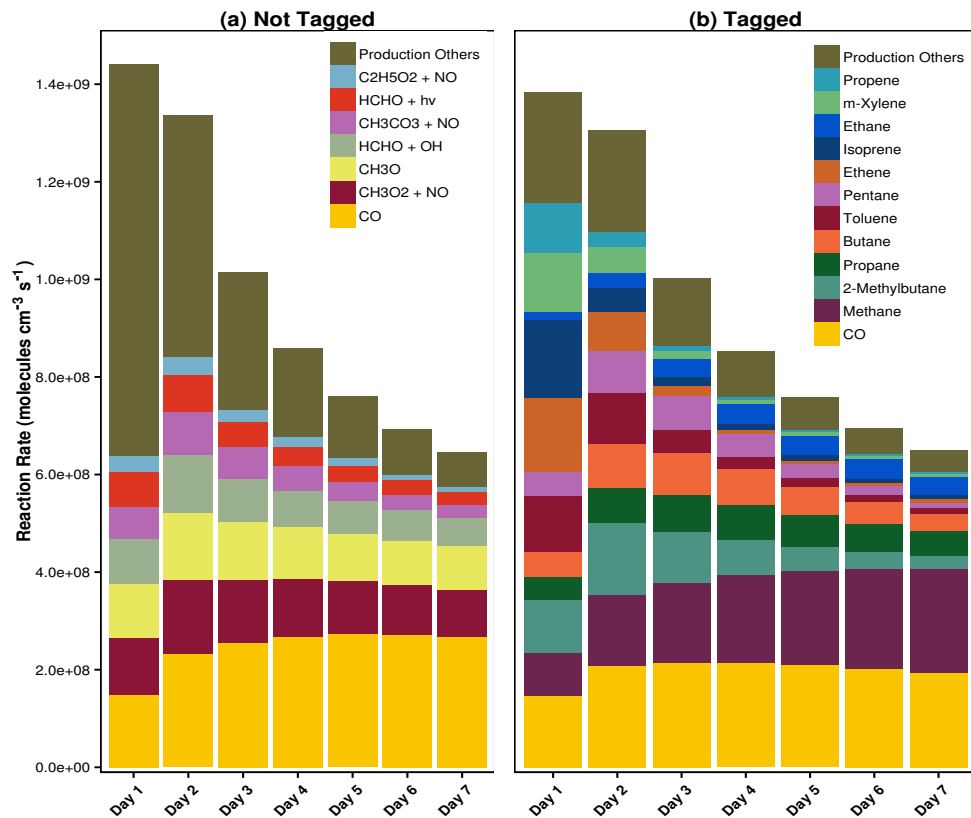


Figure S3: O_x production budget using the MCM v3.2, (a) allocated to the contributing

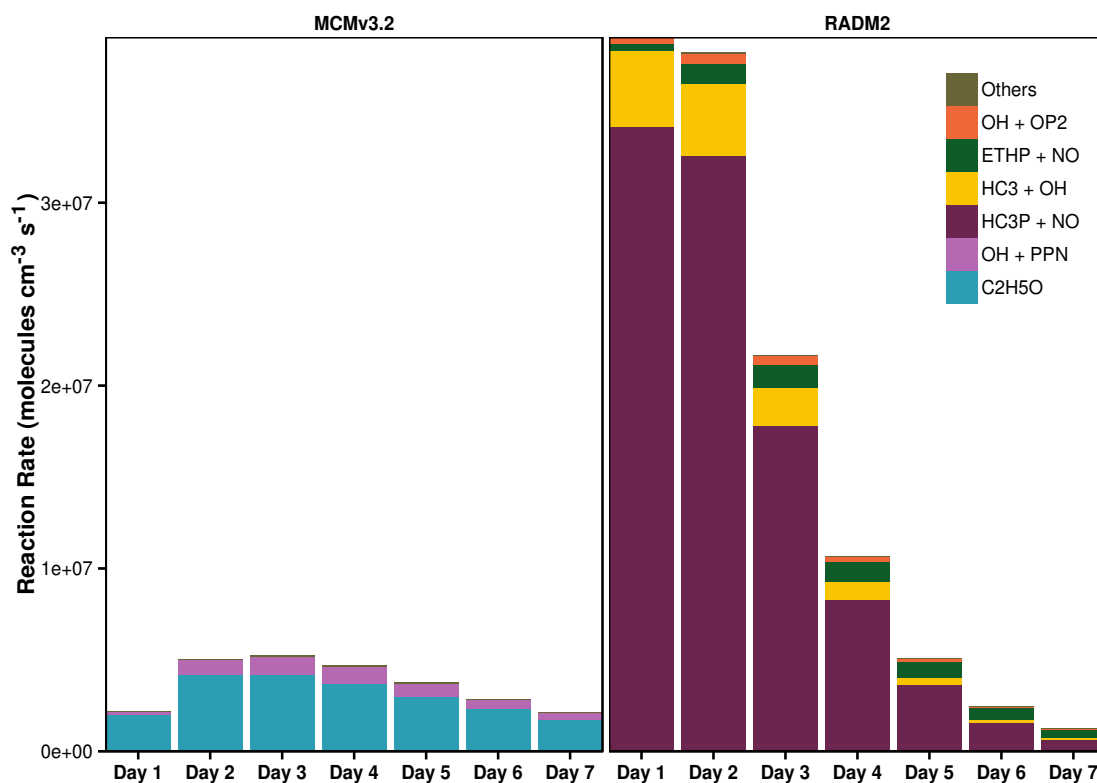


Figure S4: Acetaldehyde production budgets during propane degradation in MCM v3.2 and RADM2. The budgets are attributed to the contributing reactions.

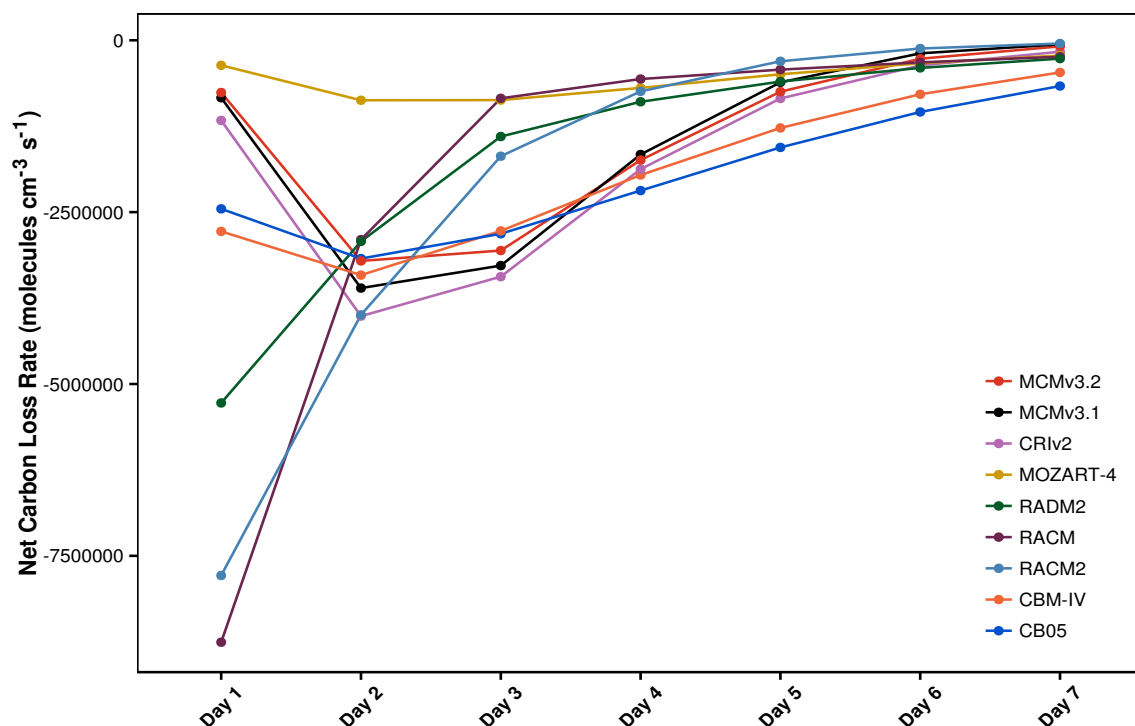


Figure S5: Net loss of reactive carbon during octane degradation in each mechanism. Octane is represented by the 5 carbon species, BIGALK, in MOZART-4.

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