



Supplement of

A comparison of chemical mechanisms using Tagged Ozone Production Potential (TOPP) analysis

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S1 Introduction

² This is the supplementary material to the research paper “A Comparison of Chemical
Mechanisms using Tagged Ozone Production Potential (TOPP) Analysis” and provides
⁴ further information about the methodology as well as additional analysis.

S2 Mechanism Setup

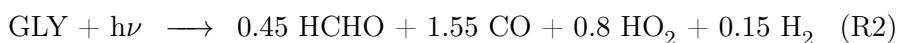
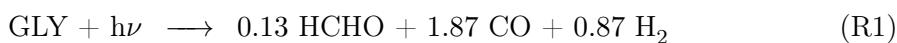
⁶ All chemical mechanisms were adapted from their original format into the modularised
KPP (Damian et al., 2002) format for use in the MECCA boxmodel (Sander et al., 2005)
⁸ as modified by (Butler et al., 2011).

The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard
¹⁰ 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.

¹² S2.1 Photolysis

Photolysis was parameterised as a function of the solar zenith angle following the MCM
¹⁴ 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.
¹⁶ 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
¹⁸ 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
²⁰ 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
²² assigned as the ONIT photolysis rate parameter in RACM2.

Photolysis reactions of a species in reduced mechanisms were sometimes represented by
²⁴ 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,
²⁶ glyoxal photolysis described by (R1) and (R2) in RADM2.



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	$k^*RO2*0.6\text{ s}^{-1}$
	C ₂ H ₅ O ₂ = C ₂ H ₅ OH	$k^*RO2*0.2\text{ s}^{-1}$
	C ₂ H ₅ O ₂ = CH ₃ CHO	$k^*RO2*0.2\text{ s}^{-1}$
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	$2 \times 10^{-13}*RO2\text{ s}^{-1}$

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.

28 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 32 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.

Reactants	Products	Rate Constant
MO ₂ + MO ₂	0.74 HO ₂ + 1.37 HCHO + 0.63 MOH	$9.4 \times 10^{-14} \exp(390/T)$ cm ³ molecules ⁻¹ s ⁻¹
MO ₂	0.37 HO ₂ + 0.685 HCHO + 0.315 MOH	$9.4 \times 10^{-14} \exp(390/T) * \text{RO}_2$ s ⁻¹
ETHP + MO ₂	HO ₂ + 0.75 HCHO + 0.75 ACD + 0.25 MOH + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T)$ cm ³ molecules ⁻¹ s ⁻¹
ETHP	0.63 HO ₂ + 0.065 HCHO + 0.75 ACD + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T) * \text{RO}_2$ s ⁻¹

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

³⁴ **S2.2 Organic Peroxy Radical Self and Cross Reactions**

Reactions of organic peroxy radicals (RO₂) with other organic peroxy radicals are divided
³⁶ into self (RO₂ + RO₂) and cross (RO₂ + R'O₂) reactions. These reactions are typically
³⁸ represented in chemical mechanisms as bimolecular reactions which would cause ambiguities
⁴⁰ when implementing the tagging scheme. Namely, which tag to be used for the products
⁴² of reactions between RO₂ reactants having different tags. The MCM v3.2 approach to
⁴⁴ self and cross RO₂ reactions (each RO₂ species reacts with the pool of all other RO₂ at a
⁴⁶ single uniform rate) is used to avoid such ambiguities. The MCM v3.2 approach represents
⁴⁸ RO₂–RO₂ reactions as a pseudo-unimolecular reaction whose rate constant includes a factor
⁵⁰ 'RO2' which is the sum of the mixing ratios of all organic peroxy radicals (Saunders et al.,
⁵² 2003).

The pseudo-unimolecular reaction products and their yields were determined by one
⁴⁶ of two methods. Firstly, by using the RO₂ + RO₂ reaction and halving the product
⁴⁸ yields, demonstrated for the MOZART-4 treatment of the ethyl peroxy radical in Table S2.
⁵⁰ Alternatively, the RO₂ + CH₃O₂ reaction was used to determine the products due to CH₃O₂
⁵² and these products are then removed.

Table S3 demonstrates the steps determining the ETHP pseudo-unimolecular reaction
⁵⁴ in RACM2. First the products due to MO₂ (CH₃O₂ in RACM2) are determined as outlined
⁵⁶ previously using the MO₂ + MO₂ reaction. The MO₂ product yields are subtracted from
⁵⁸ the ETHP + MO₂ reaction. Any products having a negative yield are not included in the

54 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.

56 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 58 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 $\text{CH}_3\text{C}(\text{O})\text{O}_2$.

60 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 ‘ RO_2 ’ factor, which is the sum of the mixing ratios 62 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.

64 Model runs using the original and modified approach to the RO_2-RO_2 reactions for each mechanism were performed. The resulting O_3 concentration time series were compared 66 and shown in Figure S1.

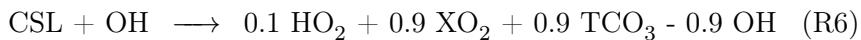
S2.3 Dry Deposition

68 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 70 mechanism species without direct MCM v3.2 analogues. For example, the dry deposition velocity of PAN-like species in all mechanisms was equivalent to that of the PAN species in 72 the MCM v3.2.

S2.4 Negative Product Yield Treatment

74 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 76 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 78 ‘NULL’ product.

For example, in RADM2 the $\text{OH} + \text{CSL}$ (cresol) reaction has negative OH yield in (R6) 80 (Stockwell et al., 1990).



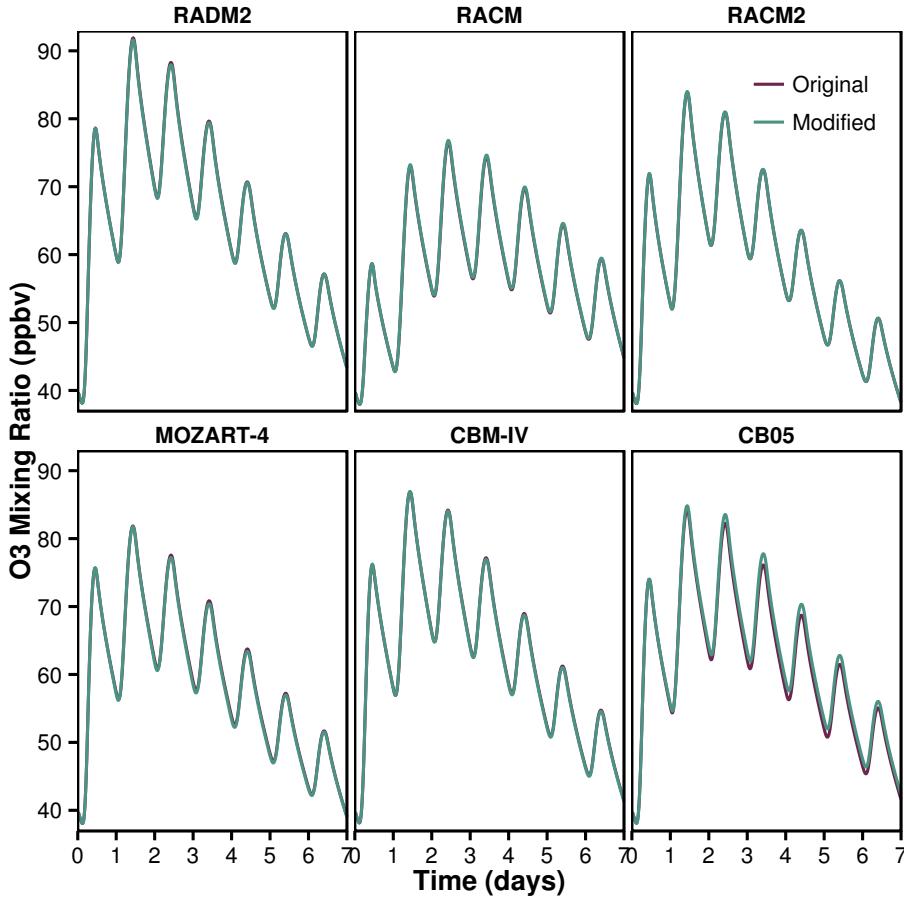


Figure S1: O_3 mixing ratio time series for each reduced mechanism using the original and modified approach to RO_2 - RO_2 reactions

82 The negative OH yield was adapted to a positive operator (OHOP) yield in (R7). OHOP
 83 then reacts immediately with OH giving a ‘NULL’ product with a rate constant of
 84 $8.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (R8). Thus preserving the OH yields from (R6) in RADM2.



86 S3 Mapping Emitted NMVOC to Mechanism Species

The emitted NMVOC are typical of Los Angeles as described in Baker et al. (2008). The
 88 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.

90 The representation of NMVOC in all other mechanisms required mapping the individual
 NMVOC to specific mechanism species. This mapping followed the recommendations on

92 the literature of the mechanism; Table S4 describes the mechanism species used for mapping
93 the initial NMVOC. Table 2 of the main article shows the final mapping of each NMVOC
94 to each mechanism species.

S4 Treatment of 2-methylpropene Degradation

96 Figure 4 of the main article shows the first day TOPP values of the VOC obtained in
97 each reduced mechanism compared to the MCM v3.2. The first day TOPP values of
98 2-methylpropene in RACM, RACM2, MOZART-4, CBM-IV and CB05 signify differences
in its degradation to the MCM v3.2.

100 The variation between RACM, RACM2 and MCM v3.2 arises from differences in the
101 ozonolysis rate constant of 2-methylpropene. This rate constant is an order of magnitude
102 faster in RACM and RACM2 than in MCM v3.2 as the RACM, RACM2 rate constant
103 is a weighted mean of the ozonolysis rate constants of each VOC represented as OLI
104 (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.

106 2-methylpropene is represented as BIGENE in MOZART-4. The degradation of BIGENE
107 produces CH_3CHO through the reaction between NO and the 2-methylpropene peroxy
108 radical, whereas no CH_3CHO is produced during 2-methylpropene degradation in the
109 MCM v3.2. CH_3CHO initiates a degradation chain producing O_x involving CH_3CO_3 and
110 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
112 PAR, the C–C bond (Gery et al., 1989; Yarwood et al., 2005). This representation of
113 2-methylpropene does not produce the 2-methylpropene peroxy radical, whose reaction
114 with NO is the main source of O_x production in all other mechanisms.

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

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

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