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*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

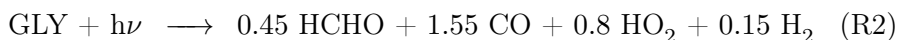
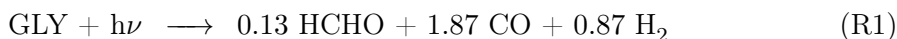
6 All chemical mechanisms were adapted from their original format into the modularised  
KPP (Damian et al., 2002) format for use in the MECCA boxmodel (Sander et al., 2005)  
8 as modified by (Butler et al., 2011).

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.



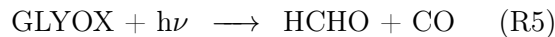
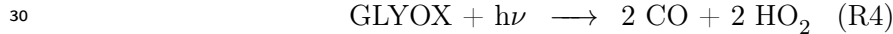
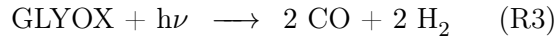
	Rate Parameter	MCM v3.2 Products and Yields
(R1)	0.87 J <sub>31</sub>	1.74 CO + 0.87 H <sub>2</sub>
	0.13 J <sub>32</sub>	0.13 CO + 0.13 HCHO
	0.87 J <sub>31</sub> + 0.13 J <sub>32</sub>	1.87 CO + 0.13 HCHO + 0.87 H <sub>2</sub>
(R2)	0.15 J <sub>31</sub>	0.30 CO + 0.15 H <sub>2</sub>
	0.45 J <sub>32</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	$k^*RO_2*0.6 \text{ s}^{-1}$
	C2H5O2 = C2H5OH	$k^*RO_2*0.2 \text{ s}^{-1}$
	C2H5O2 = CH3CHO	$k^*RO_2*0.2 \text{ s}^{-1}$
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	$2 \times 10^{-13}*RO_2 \text{ s}^{-1}$

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 RO<sub>2</sub> 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<sub>31</sub>, J<sub>32</sub> and J<sub>33</sub>.



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
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	$9.4 \times 10^{-14} \exp(390/T) * \text{RO2}$ $\text{s}^{-1}$
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	$1.18 \times 10^{-13} \exp(158/T) * \text{RO2}$ $\text{s}^{-1}$

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.

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

Reactions of organic peroxy radicals ( $\text{RO}_2$ ) with other organic peroxy radicals are divided  
36 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  
38 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 approach to  
40 self and cross  $\text{RO}_2$  reactions (each  $\text{RO}_2$  species reacts with the pool of all other  $\text{RO}_2$  at a  
single uniform rate) is used to avoid such ambiguities. The MCM v3.2 approach represents  
42  $\text{RO}_2$ - $\text{RO}_2$  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.,  
44 2003).

The pseudo-unimolecular reaction products and their yields were determined by one  
46 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.  
48 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.

50 Table S3 demonstrates the steps determining the ETHP pseudo-unimolecular reaction  
in RACM2. First the products due to MO2 ( $\text{CH}_3\text{O}_2$  in RACM2) are determined as outlined  
52 previously using the  $\text{MO2} + \text{MO2}$  reaction. The MO2 product yields are subtracted from  
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. 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  $\text{CH}_3\text{O}_2$  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  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ .

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 ‘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.

64 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 shown in Figure S1.

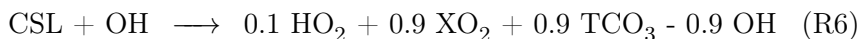
### S2.3 Dry Deposition

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



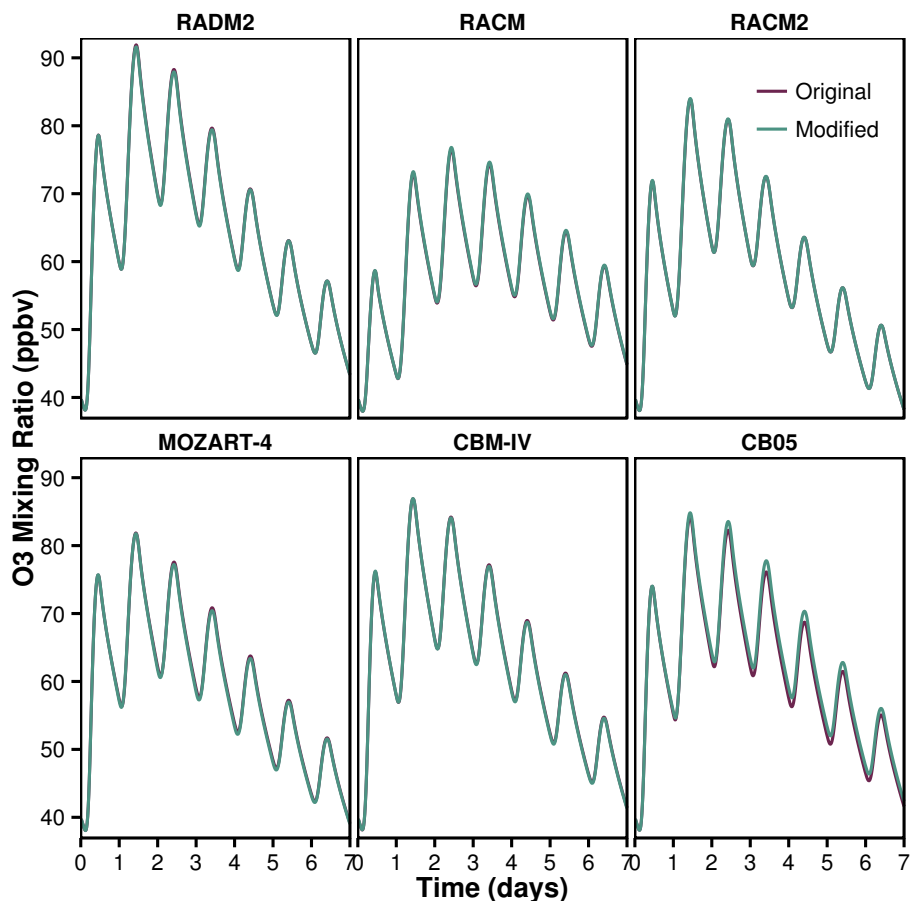
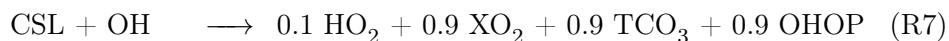


Figure S1: O<sub>3</sub> mixing ratio time series for each reduced mechanism using the original and modified approach to RO<sub>2</sub>-RO<sub>2</sub> reactions

82 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  
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  
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  
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  
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  
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  
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  
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  
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	
	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 $6.8 \times 10^{-12}$	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 $6.8 \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$	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.



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